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CHEMICAL COAGULATION/MIXED-MEDIA FILTRATION OF AERATED LAGOON EFFLUENT

J. F. Grutsch, et al

American Oil Company

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A cold weather study showed that a three-chemical destablization pretreatment system is required for filtration of biocolloids in brackish water. Determination of the optimal three-chemical destabilization system using zeta potentials required evaluation of zeta potentials in a manner which sorted out the effect of double-layer repression. The colloid destabilization mechanisms of charge neutralization and bridging were required for optimal filter performance. For colder water temperatures, even with optimal chemical treatment, the filter hydraulic loading must be decreased. The change in hydraulic loading with temperature related directly to the water's viscosity.

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by

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ABSTRACT

The applicability of chemical coagulation/mixed-media filtration as tertiary treatment for additional removal of suspended solids, oil, and biochemical oxygen demand following an oil refinery aerated lagoon has been demonstrated in a full-scale commercial unit. Two modes of operation were developed: 1) operation as a "scalping" unit, and 2) optimized operation to achieve near potable water clarity. Operation as a scalping unit in which chemical pretreatment is not optimized yields a significant improvement in many water quality parameters, particularly in the aesthetics of aerated lagoon effluent appearance. Optimized operation involves determining the requirements for chemical destabilization of the colloidal system and then responding by providing proper pretreatment.

Operating problems and the effect of operating variables were investigated during full-scale plant operations in the scalping mode. Influent suspended solids concentration and water temperature were the most significant independent variables. Mechanical limitations were studied, including a filter bed disturbance that necessitated a total bed replacement. High, localized backwash velocity caused the invisible disturbance which reduced turbidity removal from about 80 percent to 50 percent. Diagnostic procedures, design changes, and the costs of operation and maintenance are reported.

A cold weather study showed that a three-chemical destabilization pretreatment system is required for filtration of biocolloids in brackish water. Determination of the optimal three-chemical destabilization system using zeta potentials required evaluation of zeta potentials in a manner which sorted out the effect of double-layer repression. The colloid destabilization mechanisms of charge neutralization and bridging were required for optimal filter performance. For colder water temperatures, even with optimal chemical treatment, the filter hydraulic loading must be decreased. The change in hydraulic loading with temperature related directly to the water's viscosity.

This report was submitted in fulfillment of Project Number 12050 GQR, Grant Number S803026, by Amoco Oil Company, Yorktown, Virginia, under the partial sponsorship of the Environmental Protection Agency. Work was completed as of March 1974.

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SECTION I

CONCLUSIONS

1. Chemical coagulation/mixed-media filtration has been demonstrated to be an effective tertiary water treatment for accomplishing further reductions in suspended solids, oil content and biochemical oxygen demand following a refinery end-of-pipe treatment sequence consisting of an API separator and aerated lagoon.

2. The most significant factors influencing the treatment effectiveness in the scalping mode operation are incident contaminant concentration, the applied chemical treatment level, and seasonal aerated lagoon conditions.

3. Backwashing with lagoon water will keep the filter media satisfactorily free of oil and waste accumulation, and returning the backwash waste to the lagoon can be handled in a way to avoid unmanageable sludge buildup.

4. The filtration facilities require a minimum amount of operator attention and generate no objectionable wastes or odors.

5. The unit operation can be demonstrated easily, appearance of the effluent is greatly improved and the facility therefore has considerable public relations appeal. Both the process and the results are easily visible and comprehensible.

6. Unless adequate hydraulic controls are provided, the filter media can be physically disturbed, rendering it less effective than designed. Safeguards are necessary to prevent such disturbances.

7. Optimized operation to achieve near potable water quality clarity requires response to the required water chemistry for destabilization of colloidal material. This response may require taking any, or all, of the following into account: 1) pH control; 2) two or three chemical destabilization systems, and 3) reduced hydraulic loading at water temperatures less than 15.5° C (60° F).

8. Brackish water has a major impact on the effectiveness of destabilization chemicals.

9. Brackish water interferes with direct usage of zeta potentials for determining optimal chemical pretreatment because the reduction of zeta potential by double layer repression must be detected. This is readily achieved by determining zeta potentials on diluted samples.

10. Colloid entrapment and double layer repression are destabilization mechanisms to be sorted out and avoided for direct filtration.

11. Charge neutralization and bridging are required destabilization mechanisms for optimal filter performance.

12. Weakly anionic polyelectrolytes are much more effective than nonionics for filter aids in a three chemical system.

13. Even with optimized chemical pretreatment, filter loading must be decreased with decreasing water temperatures.

14. Recommended filter hydraulic loadings are proportional to the viscosity of water.

15. Incorporation of powdered activated carbon up to 150 mg/l had no favorable impact on the destabilization chemistry of biocolloids.

SECTION II

RECOMMENDATIONS

1. Future effort on this unit should include investigation and implementation of the chemical pretreatment system required to optimize performance to yield near potable water clarity for year-round operation.

2. The system variables considered in the chemical pretreatment system study should include the following: pH, multi-chemical destabilization system; zeta potential measurements; water quality parameters, and water temperature-hydraulic loading relationships.

3. An effort should be made to determine if there is enough difference in properties of inert colloids in primary effluent and biocolloids in aerated lagoon effluent to result in any practical difference in the approach to destabilization by chemical treatment.

4. Pilot plant data should be used cautiously if there is a difference between the media support and that proposed for a full-scale unit.

5. Year-round data on filterable contaminants and hydraulic requirements should be used as a design basis to set minimum design specifications if satisfactory year-round performance is required.

6. Jar tests can be used to determine the type of chemical treatment and the specific chemicals to which the waterborne colloids are most responsive, but the results should not be relied upon to predict the dosage requirements. Recognition should be made of the fact that dosage requirements will likely vary with the seasons even at the same contaminant concentration.

7. Some type of adjustable, mechanical restriction should be provided to prevent excessive backwash rates in case of instrument malfunction or operator error.

8. Design considerations involve trade-offs between hydraulic loading rates and chemical pretreatment. The more responsive the colloidal system is to chemical pretreatment the higher are the hydraulic loadings achievable. Hydraulic loadings

relate to water temperature. Recommended guideline values for granular media filter hydraulic loadings preliminary to water chemistry studies are as follows: 1.5° C (35° F) to 10° C (50° F), an overflow rate of 6.1 m/hr (2.5 gpm/sq ft); 10° C (50° F) to 15.5° C (60° F), an overflow rate of 8.6 m/hr (3.5 gpm/sq ft); 15.5° C (60° F) to 21° C (70° F), an overflow rate of 11 m/hr (4.5 gpm/sq ft; and 21+° C (70+° F), an overflow rate of 12.2 m/hr (5 gpm/sq ft).

9. Zeta potential measurements are a useful tool to determine the optimal chemical pretreatment requirements for direct filtration. Zeta potentials must be used for brackish waters in a manner that sorts out double layer repression mechanisms. Charge neutralization and bridging are destabilization mechanisms to be emphasized if optimal direct filtration results are to be achieved.

10. Brackish water systems require special attention if optimal chemical destabilization of biocolloids is to be achieved.

11. Brackish water biocolloid installations should have provision for a three chemical pretreatment system.

SECTION III

INTRODUCTION

The Amoco Oil Company Refinery at Yorktown, Virginia, has always maintained a secondary waste water treatment system for process waters and consistently discharged treated water of better quality than regulations have required. The treatment system consists of a two-cell API separator and about five acres of aerated lagoon. In 1968, permission was requested and obtained from the State Water Control Board to deepen the lagoon and add mechanical aeration. These improvements enhanced the effluent quality considerably, but the aesthetic appearance of the water did not meet Amoco's standards. The effluent was well stabilized, but contained suspended solids which imparted a gray, turbid appearance and a very slight iridescence was sometimes present.

During the summer of 1970, a pilot plant was set up to investigate the feasibility of improving the effluent appearance. In the pilot unit, alum coagulation and mixed-media filtration were successful in removing the objectionable turbidity and producing a clear effluent. In addition to the cosmetic effect, the pilot plant demonstrated considerable real value in reducing effluent oil and BOD_5 levels.

Based on the success of the pilot plant, design was begun in September, 1970, on a full-sized, mixed-media filter to treat the entire lagoon effluent. The simplicity of the design and the overall effectiveness of the treatment seemed of general interest and broad application, and Amoco applied for a Research and Development Grant from the Environmental Protection Agency, Water Quality Office. Amoco accepted a grant of not more than $73,815 on June 15, 1971, for a demonstration project, No. 12050 GQR. The stated objective of the project was to demonstrate the simplicity, ruggedness, and adaptability of chemical coagulation mixed-media filtration for producing a high quality effluent from a refinery aerated lagoon.

Mixed-media filtration may be defined as clarification of a suspension by passage through a bed of porous media that separates, and retains within the media, the solids constituting the suspension.

Historically, filtration was viewed as a polishing step following a clarifier; however, today, mixed-media filtration in the petroleum industry usually means "direct filtration." Direct filtration involves injection of required colloid destabilization chemicals with immediate transfer to the filter, i.e., there are no flash mix, flocculation, or clarification process steps prior to filtration.

The normal operation of mixed-media filters involves downward flow through the filter until pressure drop due to clogging or breakthrough of suspended matter increases to a predetermined limit. The filter is then cleansed by reversed flow fluidization after pretreatment by air scrubbing or a hydraulic surface wash.

Filter media include beds composed of sand; sand and coal; sand, coal and garnet; and other minerals and synthetic materials. Optimally, the suspension being filtered should pass through a bed of increasingly smaller pore size.

This report has been prepared to disseminate the information from the mixed-media filter study in a form acceptable to the Water Quality Office, Environmental Protection Agency.

SECTION IV

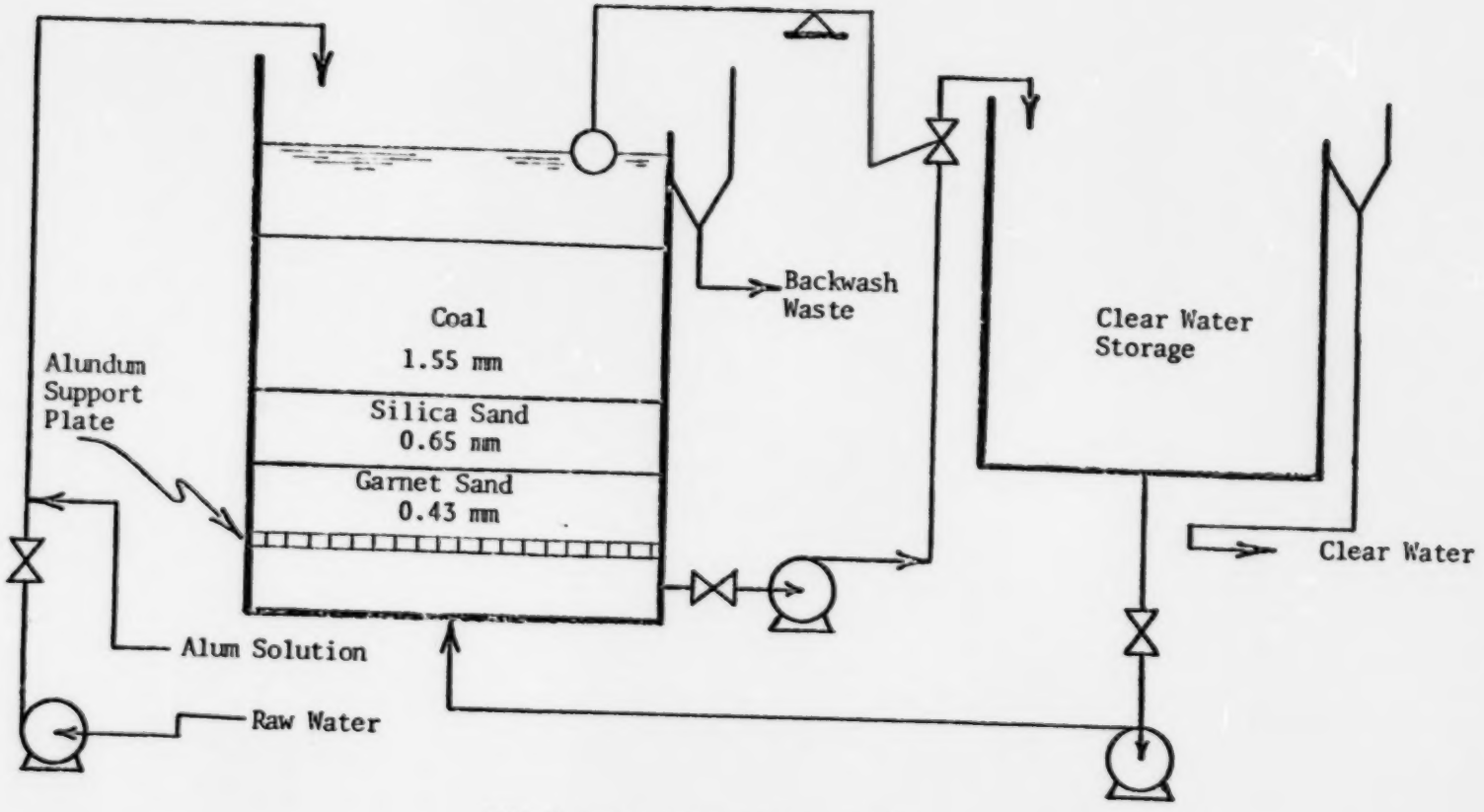
PILOT PLANT STUDIES

During the months of June, July, and August, 1970, pilot studies were conducted on the Yorktown refinery waste lagoon effluent and the API separator effluent to determine the applicability of chemical coagulation/mixed-media filtration on these streams. The pilot unit was a small, self-contained, commercial treatment system (Neptune Micro FLOC Inc., Sweet Water Boy). It consisted of a flash mix tank, tube settler, a 0.372 sq m (4 sq ft) mixed-media filter and the appropriate pumps, and controls for automatic operation. The unit had been used in extensive testing at Amoco's Whiting, Indiana, refinery and at the Texas City, Texas refinery before being sent to Yorktown. Local tests were deemed advisable to determine applicability of this unit on waters from a refinery processing foreign crude oil. The results of the tests were then logically extended to an application in a refinery at Cremona, Italy.

The flash mix chamber and the tube settling section of the pilot unit were not tested at Yorktown because of the cost-benefit data developed at Whiting. Pilot plant testing of an iron salt flocculant and/or polymeric secondary flocculants was similarly ruled out. The pilot unit is shown schematically in Figure 1. Operation entailed alum flocculation in the chamber above the filter bed, down flow filtration and clear water storage for use as backwash water. The influent water and alum rates were set and the filter level was controlled by pumping from the bottom of the unit.

Data from several of the pilot plant tests are given in Table 1. It is axiomatic that the proportion of biological oxygen demand, sulfide, phenolics, oil, or any other contaminant removed by a phase separation, such as filtration, will depend primarily upon the proportion of the specific contaminant that is insoluble in the liquid. Turbidity measurements were used to give an indication of insolubles in the pilot plant effluent and to monitor each test run continually. Spot data taken throughout the test program confirmed a rough correlation between turbidity improvement and improvement in the levels of specific contaminants. About 50 percent of the oil and biological oxygen demand were removed by the filter. The test runs were all terminated by increased filter pressure drop after 4 or 5 hours without any apparent loss of filter effectiveness. Effluent turbidity remained essentially constant throughout each test run.

Typical pressure drop data taken during one of the tests using procedures described later in this report are given in Figure 2. These data indicate that the bed is indeed an "in-depth filter." Unlike a typical sand filter, material was trapped throughout the



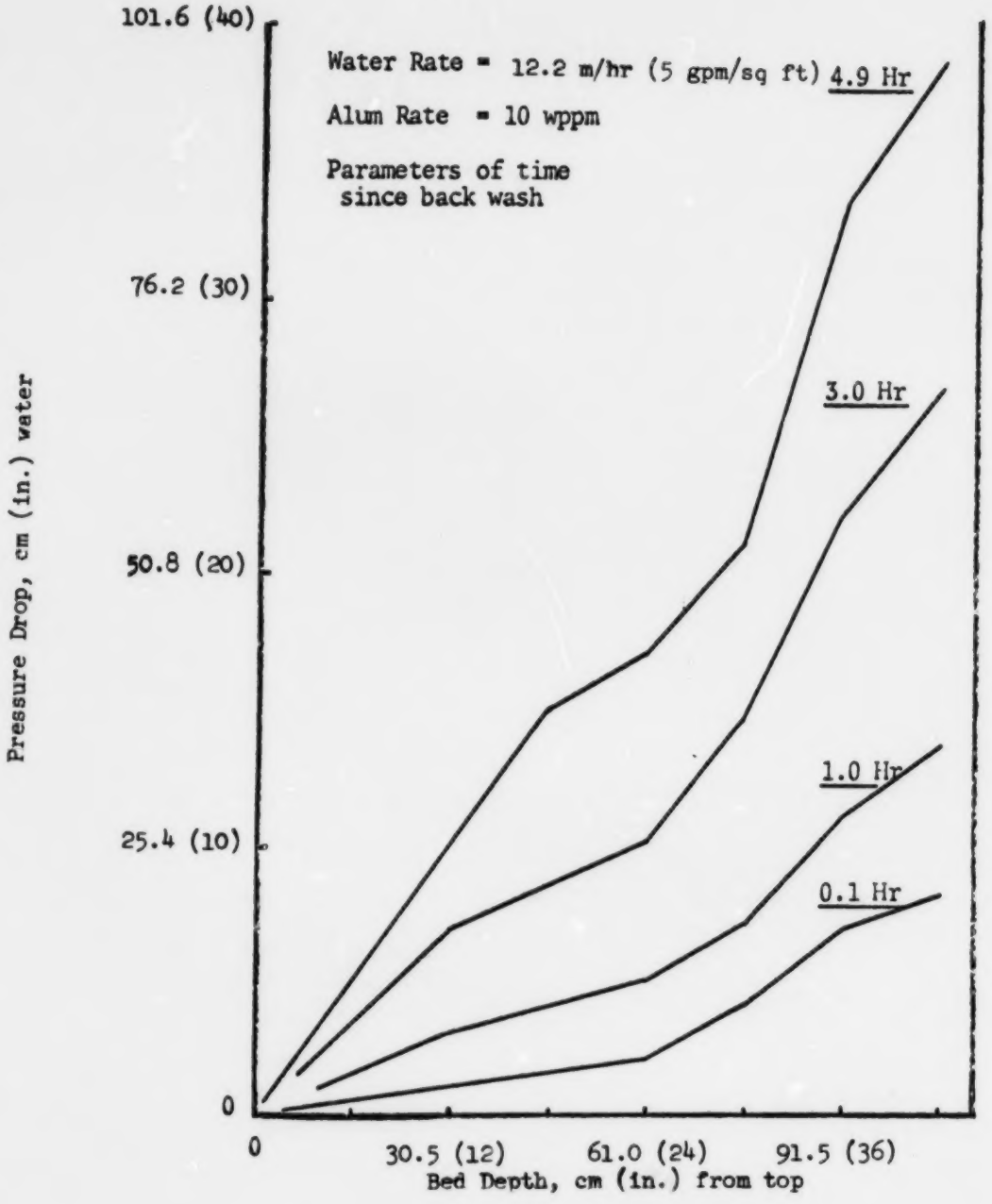
Mixed media filter pilot plant

Figure 1

Table 1. YORKTOWN WATER FILTER PILOT PLANT OPERATING AND INSPECTION DATA

Test no.	Water rate, m/hr	Water rate, gpm/sq ft	Alum rate, mg/l	Turbidity JTU In	Turbidity JTU Out	Avg oil, mg/l In	Avg oil, mg/l Out
70-1	16.5	6.75	0	11.3	8.9		
70-2	17.7	7.25	5.4	10.3	4.6		
70-3	17.7	7.25	9.0	10.3	1.9		
70-4	12.5	5.1	0	9.1	7.9		
70-5	12.2	5.0	5.0	10.9	4.6		
70-6	12.2	5.0	10.0	12.0	1.4		
70-7	6.48	2.65	5.5	8.2	4.4		
70-8	5.87	2.4	11.3	9.6	1.5		
70-21	12.2	5	10	7.1	1.5		
70-27	12.2	5	10	13.0	1.3	77	17
API separator effluent							
70-104	12.2	5	10	28	8.6	117	43
70-104a	12.2	5	15	29	4.5		14
70-105b	9.3	3.8	20	29	3.9		
70-105	12.2	5	15	25	6.3	34	20
70-106	12.2	5	15	22	4.8	12	7
70-116	12.2	5	15	21	4.6	119	24

Analytical procedures are listed in Appendix A.

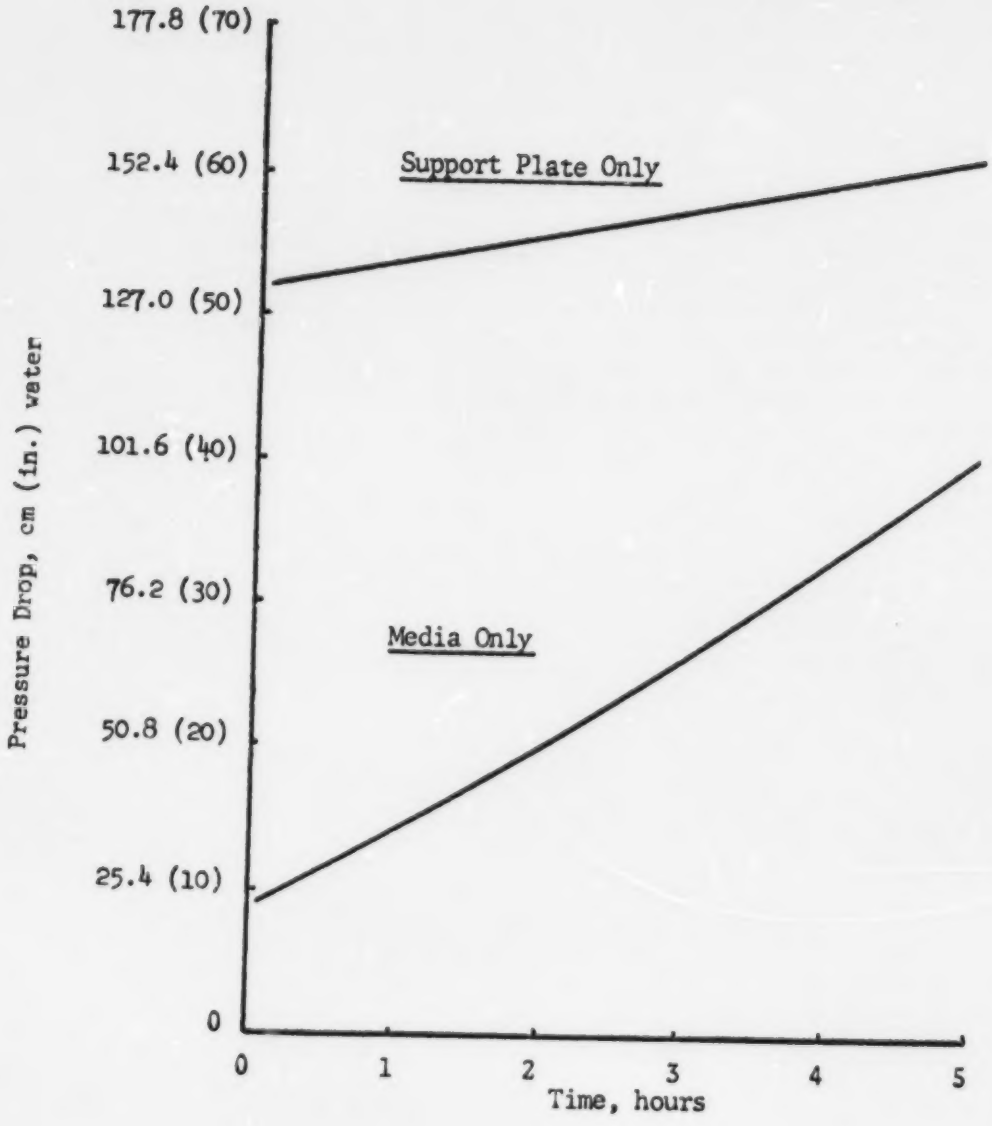


Mixed media filter pilot plant
bed pressure profiles

Figure 2

filter bed. The Alundum bed support plate also developed an increase in pressure drop as the test runs progressed (Figure 3). The effect of the support plate on effluent quality was not determined.

At the end of a test run, the effluent was shut off and the filter was backwashed at 36.7 m/hr (15 gpm/sq ft) for 6 minutes. The rate was 12.2 m/hr (5 to 10 gpm/sq ft) less than recommended, but no evidence could be found to indicate the need for a higher rate or a greater duration. Sludge settled to 5 percent of the backwash water volume in less than 2 hours and did not change volume within the next 60 days. Based on a 5-hour filter cycle at 12.2 m/hr (5 gpm/sq ft) and 36.7 m/hr (15 gpm/sq ft) for a 6-minute backwash, the backwash waste volume equalled 6 percent of the filtered water, and the settled sludge volume equalled 0.3 percent. Tests using polymeric flocculants to reduce the settled sludge volumes were inconclusive.



Mixed media filter pilot plant
pressure drop

Figure 3

SECTION V

DESIGN AND CONSTRUCTION

RESPONSIBILITY AND CRITERIA

The process design of the chemical coagulation/mixed-media filter system was the responsibility of Neptune Micro FLOC Incorporated under contract with Amoco Oil Company. They provided the automatic control mechanism, the filter media, and supervision for the media's installation. Piping and construction drawings were prepared by the local Amoco staff.

The unit was designed to treat 341 cu m/hr (1500 gpm) lagoon effluent of 9 to 12 Jackson Turbidity Units (JTU) and to produce an effluent of less than 3 JTU. Based on the pilot plant tests and the lagoon effluent data available at the time, the following reductions in contaminants were expected:

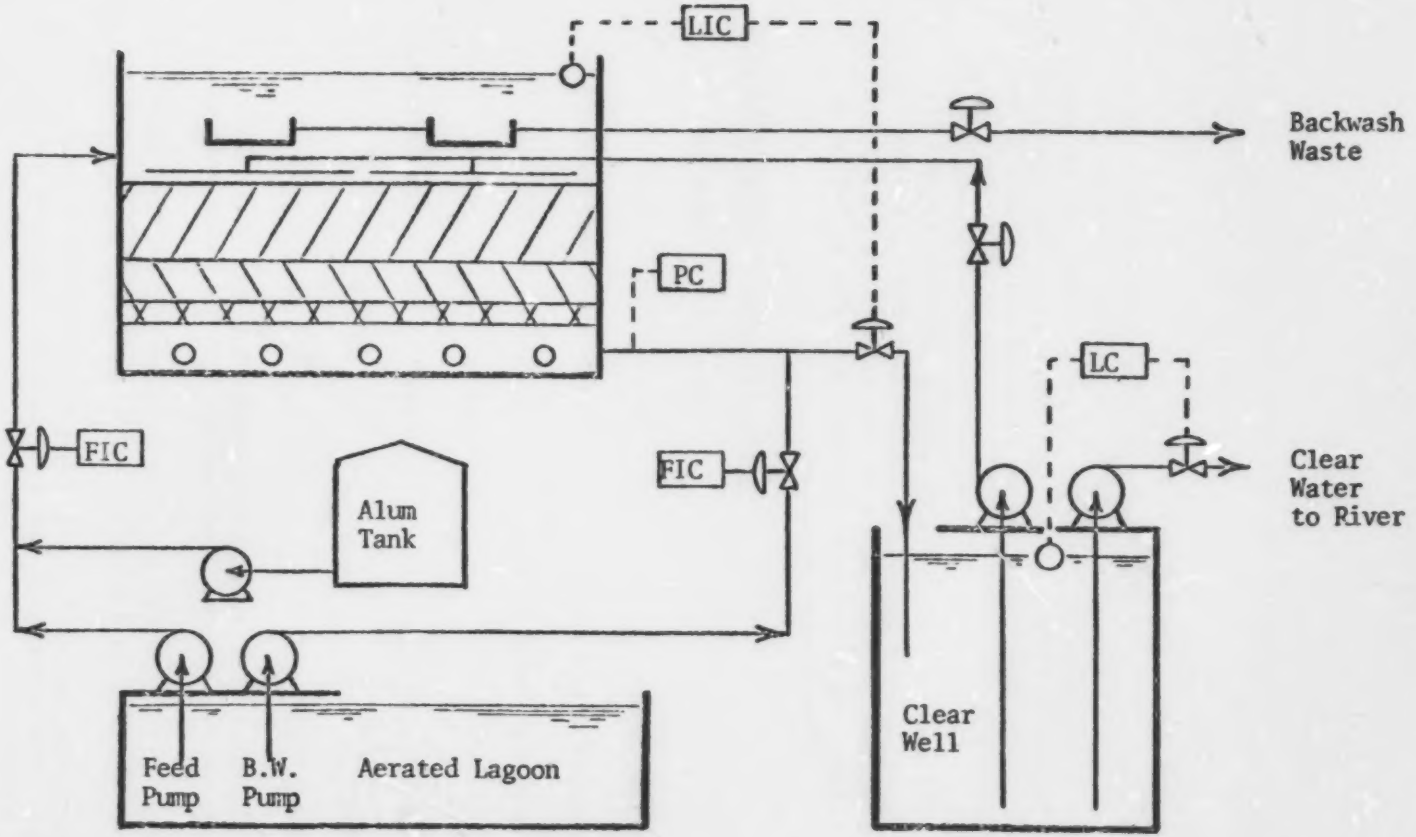
	Filter Influent	Filter Effluent
BOD_5, mg/l	7-25	*NMT 15
Suspended Solids, mg/l	5-40	NMT 3
Volatile Suspended Solids, mg/l	?	NMT 1
Oil (CCl_4 Extracted), mg/l	10-20	NMT 10
Sulfides, mg/l	NMT 1	NMT 1
Phenolics, mg/l	0-2	20% Reduction

*Not More Than

FINAL DESIGN FEATURES

A simplified process flow schematic is shown in Figure 4. The basic differences between the final design and the pilot unit were:

1. The larger unit provided 13 minutes of residence time above the bed, compared to 2 minutes in the pilot unit.
2. Two rotary surface wash arms, using filtered water, were provided. The pilot unit had a stationary surface wash but it was inoperative.
3. A plastic pipe under-drain system and graded gravel support were provided in lieu of the Alundum support plate.



Mixed media filter flow schematic

Figure 4

4. No provision was made to store filtered water for backwashing the bed. Lagoon effluent water was deemed of adequate quality to be used as backwash.

The unit was designed to operate automatically and unattended. Automatic shutdown devices were provided to prevent an overflow in the event of an equipment malfunction. A 27.9 sq m (300 sq ft) filter bed was specified, utilizing a 17.8 cm (7 in.) depth of 0.7 mm ilmenite covered with 11 inches of 1.0 mm silica sand and topped with 27.9 cm (22 in.) of 1.3 mm coal. Five pumps were specified, one each for feed, effluent, backwash, surface wash, and alum injection. Liquid alum was to be delivered by truck and stored in a 3.05 m (10 ft) diameter by 3.66 m (12 ft) high fiberglass tank. A small, clear well was provided to store filtered water for the surface wash and to allow some surge capacity for the effluent pump.

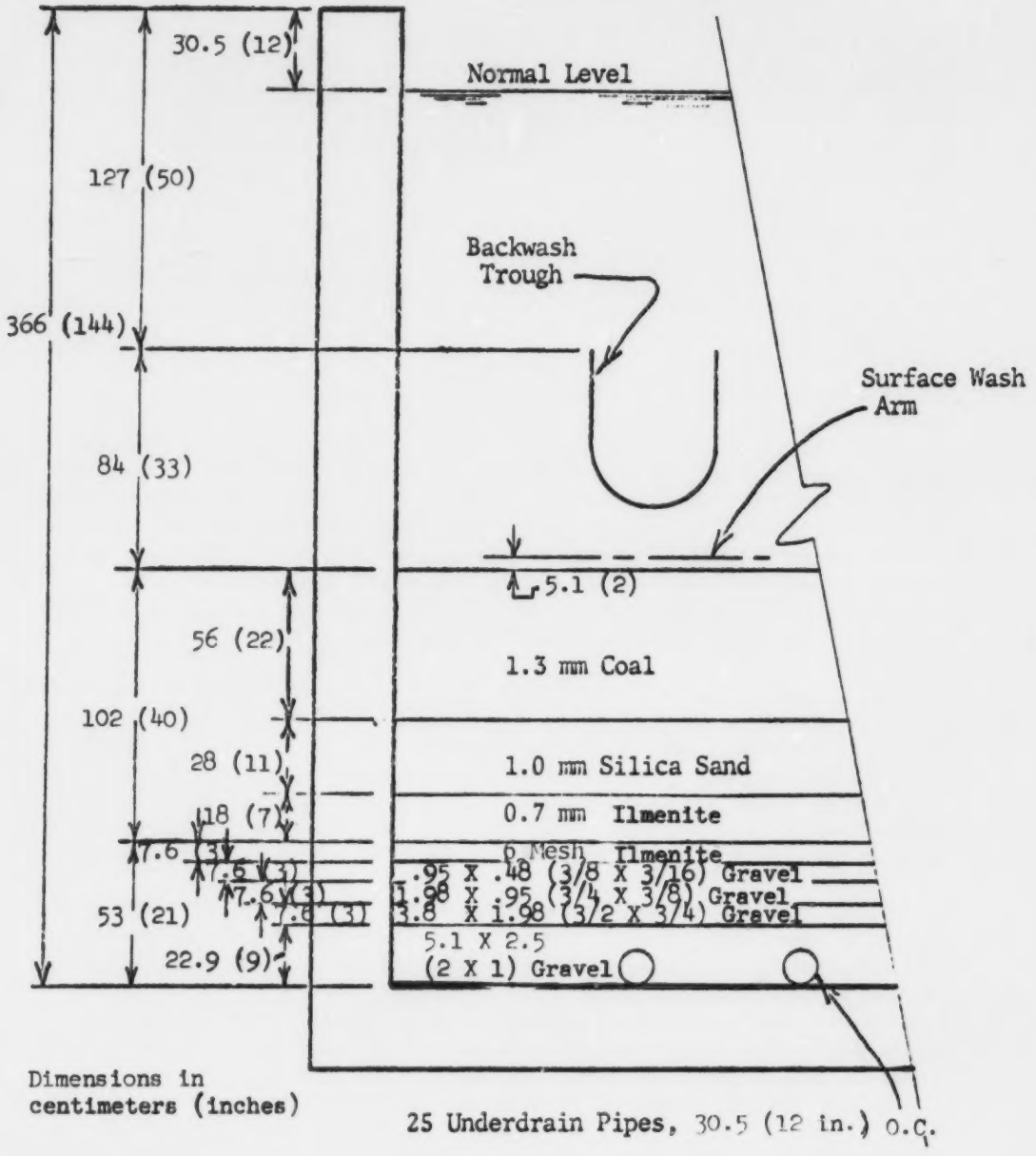
The unique feature of this design is the filter bed itself. The quality of the effluent expected from any filter design depends largely upon bed depth and media particle size. Small particle sizes produce a more clear effluent at the expense of a more rapid pressure drop build-up. Greater filter bed depth could be expected to give greater effluent quality, but the effective bed depth on a single media filter is limited by surface blinding. That is, material capable of being trapped in any specific media will be trapped within the top few inches of the bed; the remainder of the bed will then have only clear water flowing through it.

The mixed-media filter design uses three different sizes of material arranged so that the water becomes progressively more clear as it flows down through the bed. High quality effluent can be expected because of the fine particle size in the bottom of the filter. This design also gives an effective bed depth because each type of media removes some of the contaminants, and the fine particle portion of the bed is actually treating partially filtered water.

An upflow backwash would normally tend to reclassify particles of the same specific gravity, with the smaller ones on top. The specific gravities of the three bed materials in this design were chosen to prevent such normal reclassification by particle size, but enable reverse classification into 3 layers, with the small, dense particles on the bottom. Ilmenite has a specific gravity of about 5, while sand and coal are about 2.5 and 1.5, respectively. The filter bed and support design are shown in Figure 5.

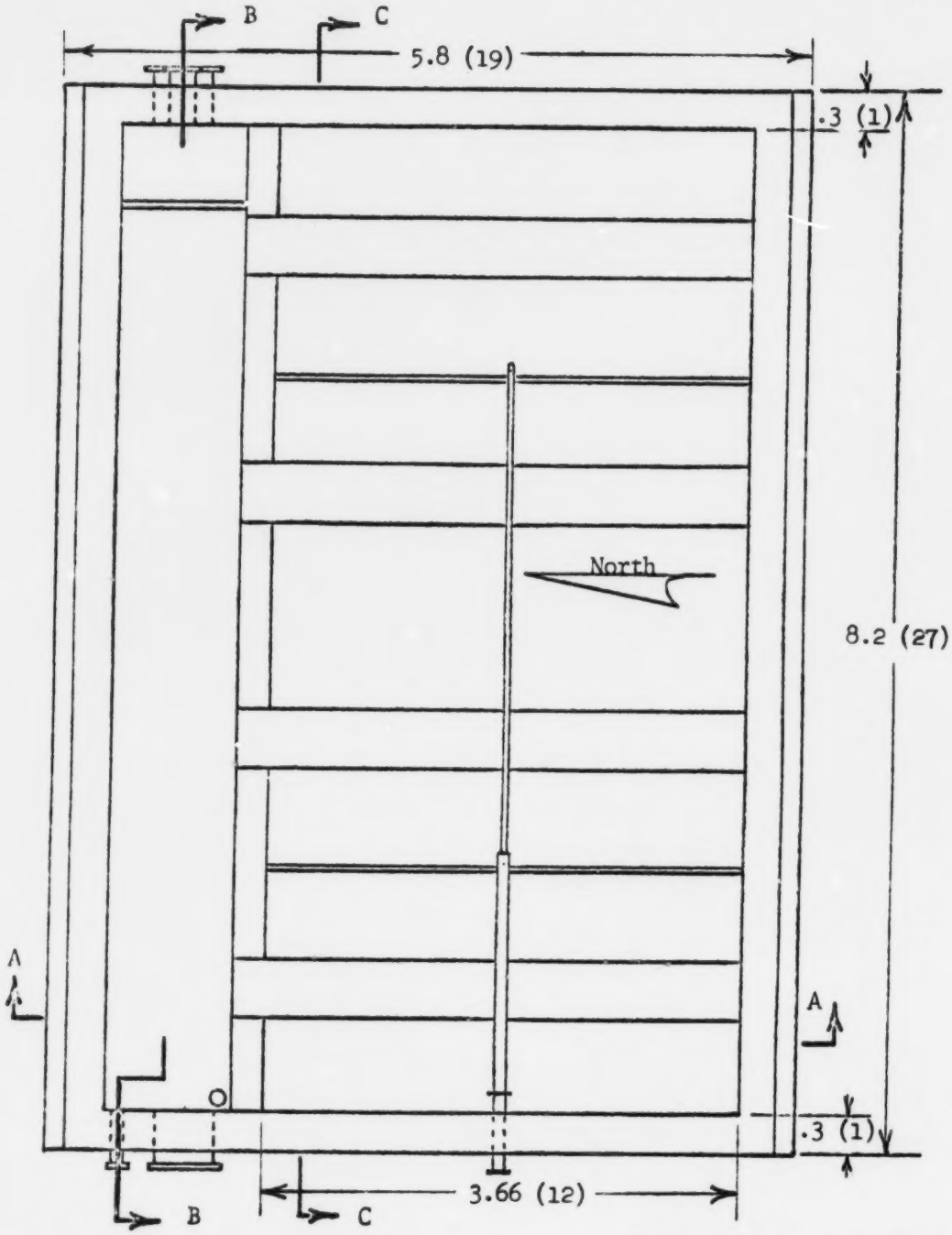
CONSTRUCTION

The unit is an open-top, reinforced concrete box, as depicted in Figures 6-9. It was built beginning in February, 1971, by Amoco



Mixed media filter bed and support design

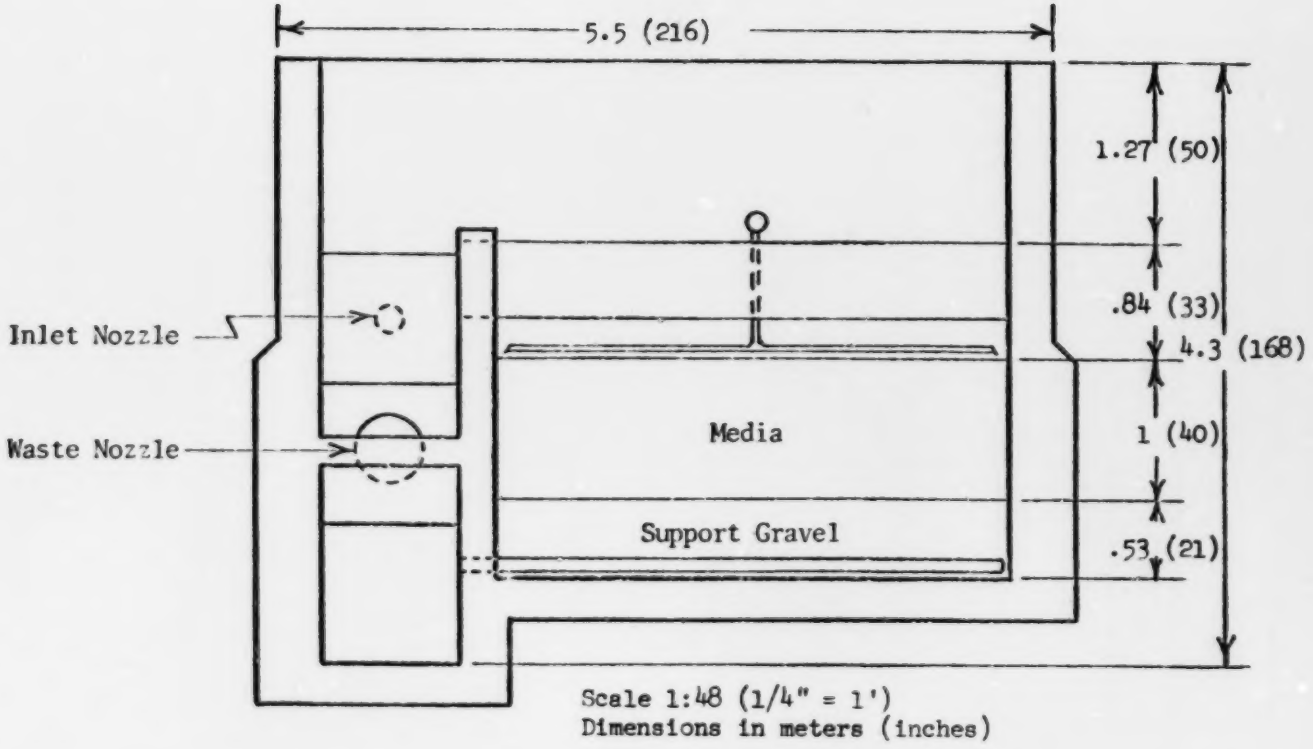
Figure 5



Dimensions are in meters (feet)

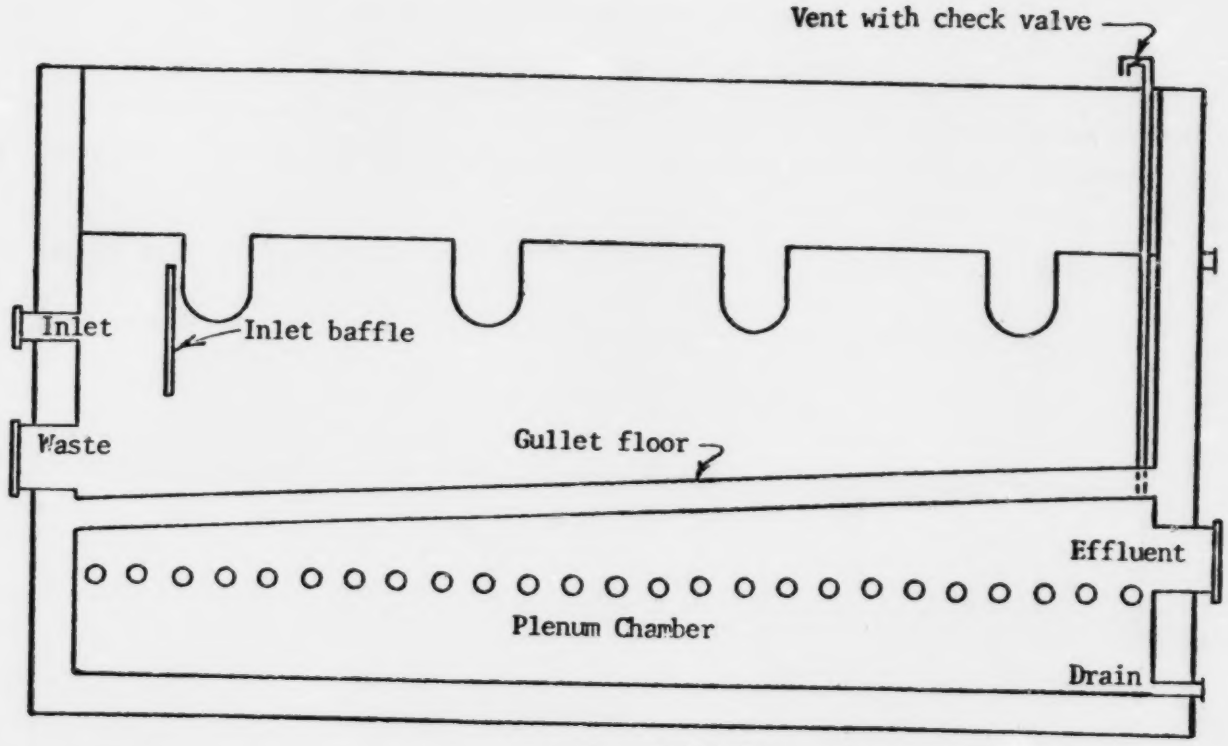
Yorktown filter plan view

Figure 6



Yorktown filter section view A-A
(looking east)

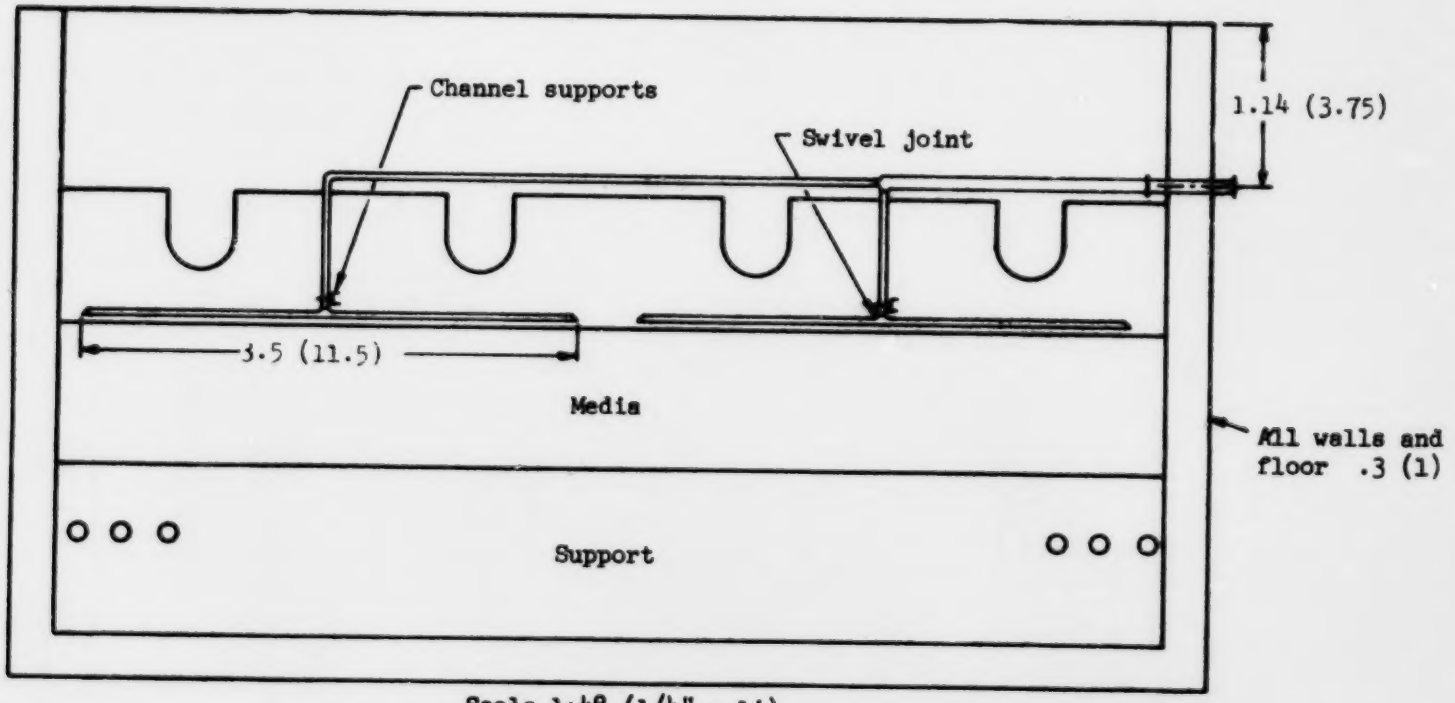
Figure 7



Scale 1:48 (1/4" = 1')

Yorktown filter section view B-B
(looking south)

Figure 8



Scale 1:48 (1/4" = 1')
Dimensions are meters (feet)

Yorktown filter section view C-C
(looking south)

Figure 9

forces and the in-plant construction and maintenance contractor Catalytic Construction Company. The construction was straight forward without any major complications or delays. On June 22, 1971, a representative from Neptune Micro FLOC began supervising the 5-day media-placement procedure. By June 29, the unit was in a usable condition with the major construction completed and only a few instrumentation problems to be solved and the weather proofing to be completed.

SECTION VI

OPERATION

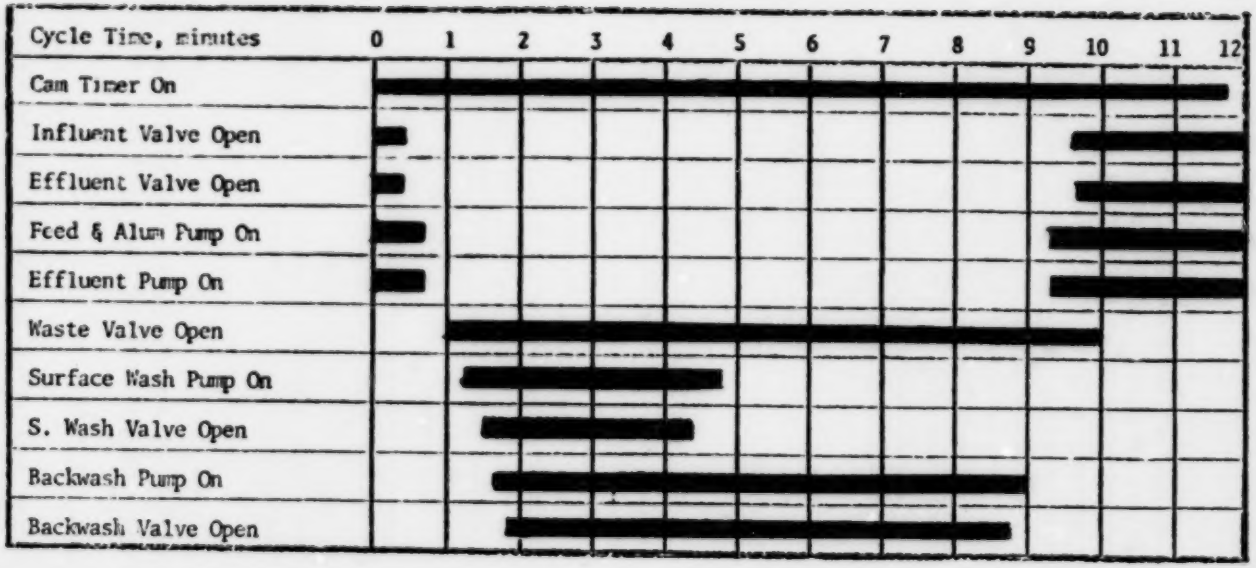
NORMAL FILTER CYCLE

The unit has been in essentially continuous operation since it was started up on June 29, 1971. The control system has functioned well, and the amount of operator attention required at the unit has been minimal. An operator normally visits the unit once per shift, primarily to inspect the equipment and to adjust the influent water rate in order to control the lagoon level. He also records the pertinent operating data at that time, including water and alum rates and effluent turbidity and pressure.

During a normal filtering cycle, water is pumped from the lagoon through a flow controller and into the filter box. The 50 percent alum solution is injected by a metering pump directly from storage tank into the line upstream of the flow controller, thus providing thorough mixing before the water enters the filter tank. Coagulation, as described later, begins immediately, and floc particles of varying sizes up to 5 mm can be seen in the gentle swirling water above the filter bed. The water flows by gravity through the media into the under-drain system and into a clear well from which it is pumped to the York River. As the voids in the media fill with material removed from the water, the differential pressure measured across the filter bed increases. Consequently, the pressure at the outlet falls. When it reaches a preset level (usually .6 m (2 ft) of water head), a multifunction timer that will automatically control a backwash is started.

NORMAL BACKWASH CYCLE

The backwashing operation is illustrated by the sequence of functions performed by the backwash timer and shown in Figure 10. After the filter influent and effluent has been stopped, the water is lowered to the level of the waste troughs by opening the waste water valve. Surface washing is accomplished by water jetting from nozzles on two arms rotating just above the bed surface. The arms operate much like an inverted lawn sprinkler, jetting about 1.2 cu m/hr (.5 gpm/sq ft) on the media surface to break up any crust that may have formed. The recommended primary backwash rate is a function of the water viscosity and varies linearly from 39 m/hr (16 gpm/sq ft) at 4° C (40° F) water temperature to 73 m/hr (30 gpm/sq ft) at 29.5° C (85° F) for the original filter design. Backwashing at this rate causes the filter bed to expand (covering the surface wash arms) and



Filter backwash cycle timer functions

Figure 10

release the entrapped waste. The partially-fluidized, expanded bed tends to be self-scouring. The timer begins another filter cycle at the end of each backwash and then deactivates itself.

OPERATING DATA

Averages of operating and analytical data for the various periods of this study are given in Table 2. Based on previous data, the incident contaminant load was unexpectedly high and variable. On several occasions, particularly during the March-May quarter, the lagoon water became very milky and exhibited turbidities up to 300 JTU. Turbidity data from these periods have been excluded from the averages as unreliable and nonrepresentative. The milky condition is believed to have been caused by a colloid (possibly sulfur) which resulted from the oxidation of a dissolved contaminant in the water. Filter effluent turbidity was virtually impossible to measure during these periods because it changed during the sampling and measuring procedures. Material that passed the filter in a dissolved state became oxidized as the samples were drawn and the resulting colloid produced a turbidity that continued to increase for up to two hours.

Again, it is important to note that the removal of any contaminant from the water is dependent not only upon the efficiency of flocculation and filtration as measured by suspended solids or turbidity removal but also upon the extent to which that contaminant is dissolved in the water. For example, the gradual deterioration of filter performance over the first four periods is not evident from the sulfide removal data. The increase in dissolved oxygen can be attributed to the exposure of water from the bottom of the lagoon to the air in the shallow, open-filter tank.

Significant data from the summer of 1972 are not available because the grant period had expired. The filter bed was obviously displaced, however, the unit was in continuous operation during the period and effecting a beneficial change on the lagoon effluent, but laboratory documentation was not obtained.

CHRONOLOGY

A chronological listing of events pertinent to the unit operations, modifications, and evaluation is given in Appendix B.

CHANGES FROM ORIGINAL DESIGN

No significant changes have been necessary in the original mode of operation. The backwash flow rate correlation was changed

Table 2. YORKTOWN MIXED MEDIA FILTER AVERAGE OPERATING DATA AND LABORATORY ANALYSES

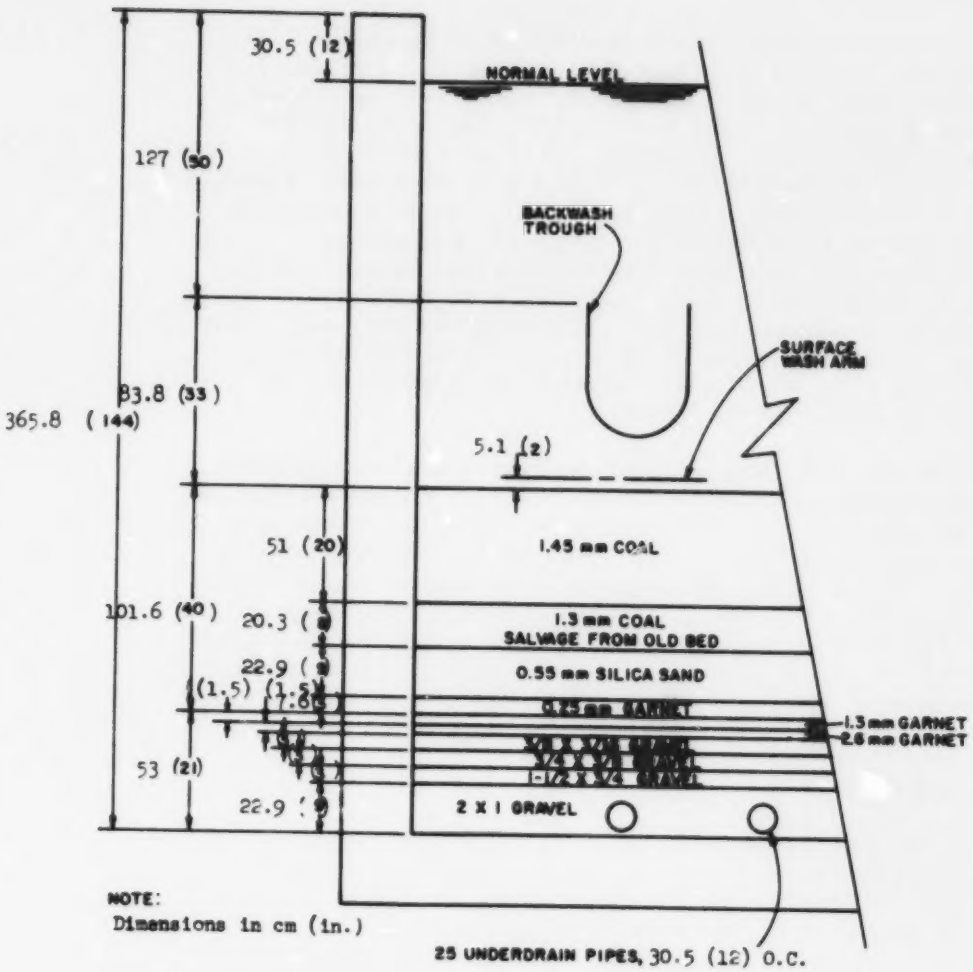
Quarter ending	Sept. 1, 1971		Dec. 1, 1971		March 1, 1972		June 1, 1972		Dec. 6, 1972	
Data from appendix	C		D		E		F		G	
	Inlet	% Removed	Inlet	% Removed	Inlet	% Removed	Inlet	% Removed	Inlet	% Removed
Water rate, cu m/hr (gpm)	255 (1125)		331 (1456)		332 (1461)		296 (1304)		343 (1510)	
Alum rate, wppm	20.0		24.4		29.4		31.6		21.2	
Water temperature, °C (°F)	27 (81)		20.5 (69)		10.5 (51)		15.5 (60)		18.5 (65)	
Turbidity, JTU	20	84	32	79	65	63	68	47	33	67
Oil, mg/l	7	73	16	49	16	38	17	22	9	36
Phenolics, mg/l	1.1	73	0.7	34	0.5	20	0.9	14	0.6	29
Sulfide, mg/l	0.7	14	3.1	26	0.9	33	1.0	50	0.9	54
pH	7.1		7.0		7.4		7.5		7.3	
Suspended solids, mg/l	18	73	43	68	68	43	69	45	90	53
Volatile sus. solids, mg/l			35	71	50	42	50	40		
Ammonia, mg/l			54	1	55	0	52	3		
Dissolved oxygen, mg/l			1.4	-39	2.6	-62	0.7	-65		
BOD_5, mg/l	35	54	19	44	18	39	34	12	18	29

when an error was discovered in the original instructions, and again when the media was changed, but the basic method of operation has been satisfactory.

Several minor equipment changes have been necessary. Thin redwood strips have been bolted to the edges of two of the backwash troughs to compensate for level differences between troughs and equalize the waste flow distribution into the gullet. A .84 sq m (9 sq ft) redwood impingement baffle was installed in the gullet to prevent displacement of the top media layer as described later. A secondary flocculent nozzle was mounted on the impingement baffle pointing into the center of the influent nozzle. The continuous recording turbidimeter which was originally mounted inside the control cabinet was remounted on the control building wall to provide easier access and prevent moisture from affecting electrical circuitry.

The most significant modification of the original design was a complete changeout of the filter media and gravel support. The replacement was necessary because the original bed had become severely disturbed. Support gravel (2.5 cm) was found in the sand layer and most of the ilmenite and some of the sand had migrated through the support and under-drain laterals into the under-drain plenum. The vendor indicated that only four or five such failures had been observed in four to five thousand units.

The new bed was an advanced design as shown in Figure 11. It provided a finer media for the bottom layer to improve effluent quality without additional head loss because the upper layers of media were redesigned to collect a larger percentage of the contaminant. The new design had the added advantage of requiring a lower backwash rate. Thus, it eliminated the need to replace an undersized waste water effluent nozzle. Responsibility for the bed replacement was shared, the manufacturer supplying the material and technical assistance, and Amoco supplying the labor. The approximate costs were $4,000 for material, $2,000 for freight, and $1,250 for five days technical help. Labor costs included three laborers, a foreman and a crane operator for ten days. Five days were required to remove the old bed and clean the areas between the under-drain laterals, and five days were required to lay the new bed.



Scale 1:48 (1/4 in. = 1 ft)

Mixed media filter bed and support, second design
Figure 11

SECTION VII

TESTS AND OBSERVATIONS

MEDIA SURFACE DISTURBANCES

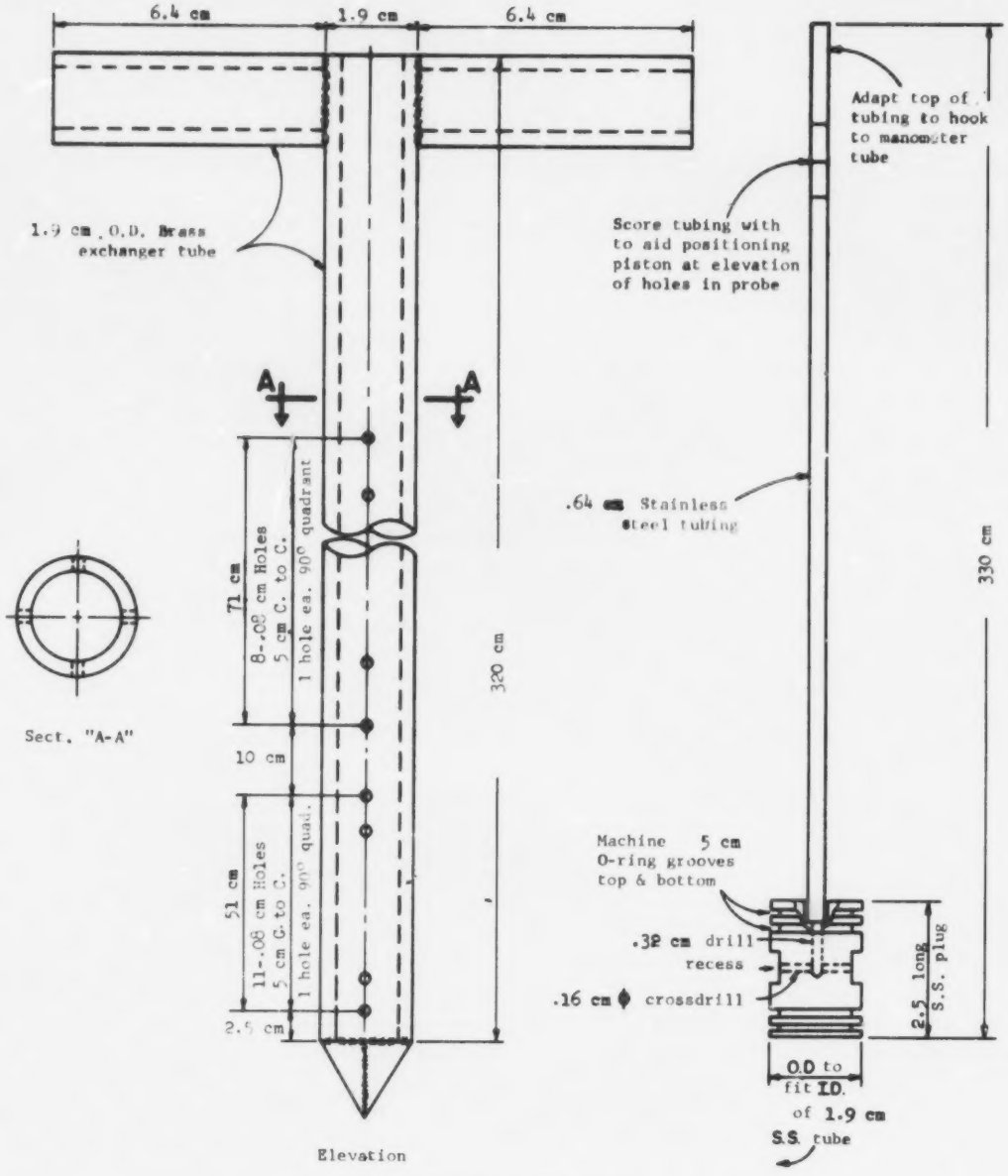
On several occasions when the media was purposely exposed, a bed disturbance was noted that involved about one-third of the bed surface. Coal from the west end of the south wall had been deposited in a mound over the west surface wash area leaving a hole 51 cm (20 in.) below the original bed surface (Figures 6 and 7). This coal displacement was determined to have been caused by the influent water during normal operation. Water entered the filter from the east, traveled 7.6 m (25 ft) and impinged on the west wall. From there the water moved over the gullet wall and 4.6 m (15 ft) on the south wall, and then down about 1.5 m (5 ft), impinging on the bed surface and displacing the coal. The surface was completely restored by a normal backwash so that the disturbance was only evident if the unit was drained before backwashing (not usually the case).

The effect of the coal displacement on filter effluent quality could not be documented, but pressure profiles indicated that the areas of the bed where the hole and mound would be formed did about equal work immediately after a backwash, before the coal had been completely displaced. The hole in the bed did provide a minimum resistance path for the backwash water. Evidence of high velocity could be seen on the water surface in the southwest corner during the first minutes of a backwash. A redwood splash baffle directly in front of the inlet nozzle completely eliminated the bed disturbances.

MEDIA PRESSURE PROFILES

Media pressure profiles were taken from different locations in the bed with a probe, shown in Figure 12. One leg of a manometer was connected by transparent flexible tubing to the small tube in the probe. Tubing from the other leg was weighted and allowed to hang below the water surface in the filter. Then, by inserting the probe into the bed and positioning the piston opposite the probe holes at the desired depth, the pressure drop from the surface to that depth could be read directly on the manometer.

The total head loss from the filter surface to the pressure switch on the filter effluent was never accounted for by probe measurements of the media. The head loss unaccounted for, about .46 m (1.5 ft) of water at 341 cu m/hr (1500 gpm), remained essentially constant. It was assumed to have been partially due to pressure drop through the support under-drain system and


6.4 cm
1.9 cm
6.4 cm
1.9 cm O.D. Brass exchanger tube
A
A
71 cm
8-.08 cm Holes 5 cm C. to C.
1 hole ea. 90° quadrant
320 cm
10 cm
51 cm
11-.08 cm Holes 5 cm C. to C.
1 hole ea. 90° quad.
2.5 cm
Sect. "A-A"
Elevation
Adapt top of tubing to hook to manometer tube
Score tubing with to aid positioning piston at elevation of holes in probe
.64 cm Stainless steel tubing
330 cm
Machine 5 cm O-ring grooves top & bottom
.32 cm drill recess
.16 cm crossdrill
2.5 long S.S. plug
O.D. to fit I.D. of 1.9 cm S.S. tube

Porous bed pressure probe
Figure 12

partially due to measurement error induced by a wall effect on the probe itself. The success of the media design at "in depth" filtration can be inferred from profiles as shown in Figure 13. Head loss developed at all levels of the media as filtration progressed.

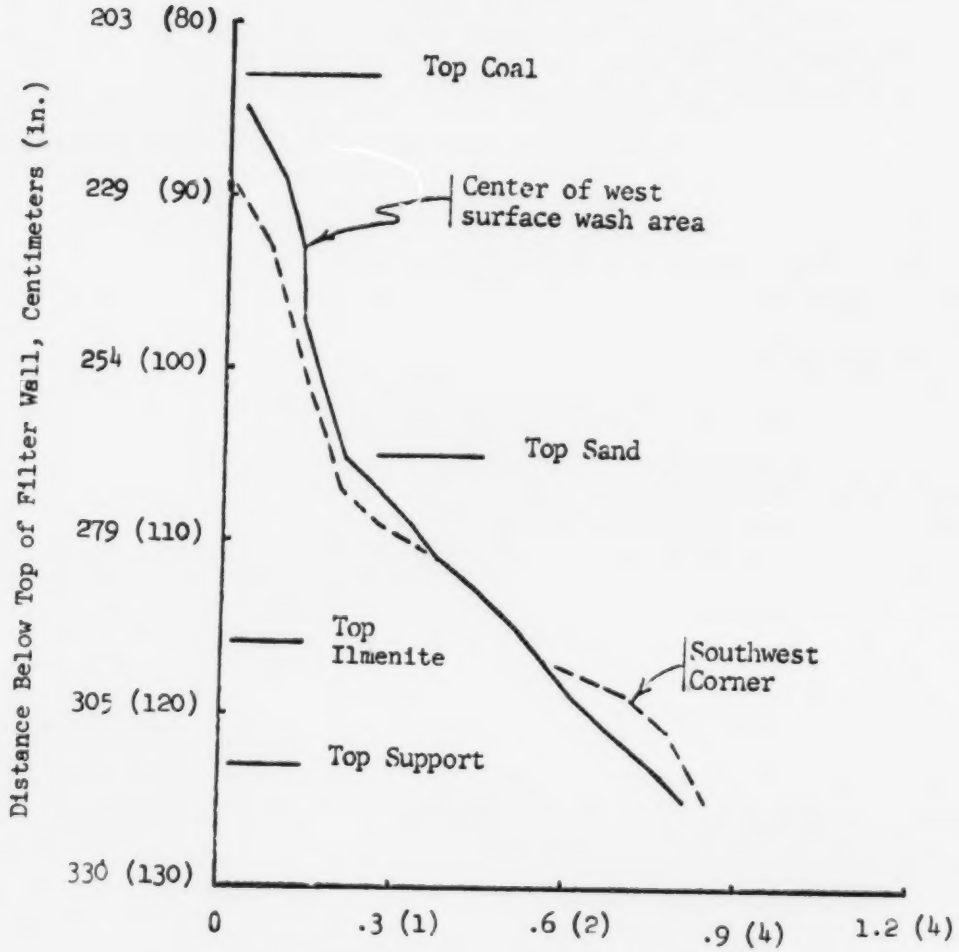
BACKWASH TIME AND WATER RATE

The recommended backwash flow versus water temperature relationship that was supplied with the unit was in error. As a consequence, all the backwashes for the first four and one-half months of operation were about 65 percent of the intended rate. Effluent quality during this period was poorer than expected from the pilot plant but the percentage of contaminant removal was only slightly less than expected. There was no significant improvement in contaminant removal after the backwash rate was increased. Head recovery was increased about 50 percent to 1 m (3 ft) of water by the more vigorous backwashing, thus filter run lengths were increased 50 percent.

The filter bed had expanded, raising the surface about 5 cm (2 in.) within the first two months of operation. The bed surface subsequently dropped 17.8 cm (7 in.) to 12.7 cm (5 in.) below the original level after the higher backwash rate was put into practice. On the erroneous assumption that coal was being backwashed out of the bed, the surface wash cycle was set to terminate before the backwash valve had reached its maximum opening. The quantity of coal that could be seen flowing into the waste troughs (less than a handful per backwash) was not affected by the change in surface wash. The manufacturer reported that a small loss of coal was to be expected with the higher rate.

Visual observation of the waste water flowing into the backwash troughs indicated that most of the material trapped in the bed was released between one-half and five minutes after the backwash valve was opened. The minimum acceptable backwash time was determined by observing the head recovery on backwash for two successive filter cycles. The first backwash observed for this test was the shorter of the two and was of the same duration that had been set up as standard operation a week earlier. The second cycle was given the designed seven minutes. Head recovery after a five-minute backwash was within 6 cm (2.4 in.) water of that after a seven-minute wash.

Because the Yorktown filter uses lagoon effluent water for backwash and returns the waste to an upstream portion of the lagoon for settling, there is only a minimum penalty for extending the backwash time. It has been left at seven minutes. If, however, filtered water were being used for backwash water, the reprocessing would consume valuable filter capacity and the backwash time would have been lowered to about five minutes.



Effect of surface disturbance on Yorktown mixed media filter

Figure 13

OIL CONTAMINATION

During October, 1971, a torrential rain flooded the API separator and produced an oil slick on the lagoons. Free oil was pumped onto the filter during normal operation and up through the filter during backwash. Oil from the backwash apparently coated the media and was subsequently partially flushed out by the filtered water to form a slick in the effluent sump for the next several hours. Oil removal efficiency of the unit remained good in spite of the oil soaked condition of the media. Routine samples taken during the next week had 62 and 87 mg/l oil in the influent water and 9 and 23 mg/l in the effluent. Media samples taken ten days after the initial contamination showed coal with 200 and 330 wppm oil and silica sand with 60 wppm. Forty days after the incident, no oil could be found on the coal.

During the week following the rainstorm, and at other times when the filter influent oil level was high, the backwash waste contained free oil. Oil that was invisible in the influent water was apparently agglomerated into floc particles that subsequently broke up and released larger oil droplets that were visible on the backwash waste water.

MEDIA SAMPLING

Attempts at core sampling with plastic pipe proved unsuccessful with 2.5 cm (1 in.) and 5 cm (2 in.) pipes held either vertically or on an angle. In general, if the media was fluid enough to enter the sampler without distortion, it would fall out the free end as the sampler was withdrawn from the bed. All media samples were obtained by digging through the coal to the sand. Then, while standing on the sand, the investigator obtained samples of the lower two layers of media by using a clam-shall type posthole digger. Extreme care was necessary to prevent disturbing the top support layer.

MEDIA SUPPORT DISTURBANCES

About four months after the proper backwash rate was initiated, four holes were dug in the bed to confirm the extent of media loss. In each case, the coal layer was about 53 cm (21 in.) deep (originally 56 cm (22 in.)) and had a sharp line of demarcation between it and the sand layer. The sand and fine garnet layers (originally 28 cm (11 in.) and 17.8 cm (7 in.), respectively) were not distinguishable as separate layers, but appeared as 40.6, 48.3, 38.1, and 43.2 centimeters (16, 19, 15, and 17 in.) of sand in the four respective holes. The top two support layers 7.6 cm (3 in.) coarse garnet and 7.6 cm (3 in.) of .95 x .48 cm (3/8 by 3/16 in. rock) were mixed in a layer from zero to 12.7 cm (5 in.) thick. A small coal loss to the backwash waste had been expected, but the 12.7 cm (5 in.) drop in the bed surface seemed to have come from the top support layers.

Three tests were conducted to determine the extent of the support loss. A .64 cm (.25 in.) diameter rod was pushed into the bed at each intersection of a .3 m (1 ft) by .3 m (1 ft) grid while the filter was operating in a normal manner. The rod was forced down until the support layer was felt, and the length of the rod below the water level was noted. The readings obtained in this manner are somewhat subjective but were found to be reproducible within about 5 cm (2 in.). The surface of the support was not flat and did not remain constant. In the first test the maximum reading was 20 cm (8 in.) above the original level and the minimum was 20 cm (8 in.) below with the average of 312 readings being 5 cm (2 in.) below the original level. Three weeks later the extremes were 22.9 cm (9 in.) above and 20 cm (8 in.) below, with an average of 7 cm (2.75 in.) below. The high spots and the low spots did not necessarily appear in the same places during the two tests. The maximum difference between two adjacent readings (.3 m (1 ft) apart) was 30.5 cm (12 in.).

At the suggestion of the filter manufacturer, a 12.7 cm (5 in.) by 15.2 cm (6 in.) plate was welded to the end of a rod and the apparatus used as a probe to determine the level of the support layer during a backwash. The extreme readings were 38 cm (15 in.) above and 20.3 cm (8 in.) below the original, with the average about 2 cm. (.75 in.) below original. The maximum variation between adjacent locations was 51 cm (20 in.). At several of the locations where the support was recorded more than 30.5 cm (12 in.) above original level, the probe felt as if it were resting upon a steep mound of mud. No physical evidence of these "mud hills" could be found in the two locations opened by coring at that time. In fact, no mud was ever found in the bed during the approximately one dozen samplings, or during any other investigations.

A possible explanation for the phenomenon of feeling "mud hills" when none were there was suggested during a visit of the manufacturer's representative, but it was never proved. The underdrain system was designed to have a 4 m (13 ft) water head loss at 1840 cu m/hr (8100 gpm) backwash rate. It actually exhibited a 5 m (16.5 ft) water loss at only 1567 cu m/hr (6900 gpm). This indicated a flow restriction that was postulated to have caused localized high velocities similar to a subsurface fountain. These fountains or jets might have had enough force to tend to support the probe if it were restrained from "sliding off the hill". The under-drain system was later proved to be unrestricted, but part of the support gravel was packed with finer gravel and sand thereby restricting flow through the support.

Another probe was constructed using .64 cm (.25 in.) mesh screen instead of the steel plate. It was unavailable to test the water jet theory, but later proved unsatisfactory in probing the replacement

filter bed. The bars that were used to stiffen the screen formed a basket and trapped support and media on top of the screen. Its use was discontinued to prevent a possible mixing of the support media in the new bed.

The downward migration of the media and the disturbance of the original support were determined to be critical and irreparable, and the entire bed had to be replaced. The reason for the problem is believed to have been localized, high backwash velocity.

Several causes for high velocity in the bed were postulated but none could be proved. The probability of air in the backwash was slight because the air vent had been functional since the startup. The possibility of poor distribution because of the broken under-drain pipe was eliminated by inspection during the bed changeout. Another theory is that mud balls were formed during the early weeks of operation when the surface wash arms were not functioning, that the mud caused poor backwash flow distribution and gravel displacement, and that the mud was broken up and eliminated by the surface wash when it was put into service. This theory seems unlikely. A more plausible explanation would be that the backwash rate which was set by the manufacturer and limited by an under-sized backwash waste nozzle was inadequate to clean the bed. The large surface depression created by the inlet water turbulence before the baffle was installed afforded a low resistance channel to pass an inordinate portion of the backwash water. This, then, reduced the cleansing in the remainder of the bed and the situation compounded itself until the localized velocity was sufficient to carry gravel up into the filter media. With the gravel support disturbed, the finer media and support then migrated down into the coarser layers and eventually through the under-drain laterals. About 1.53 cu m (2 cu yds) of fine media were found in the plenum during the bed changeout.

OIL DISPERSANT TEST

Laboratory analyses had indicated that oil dispersants or surfactants that at one time were used to wash down equipment would cause a milky appearance in the API separator water. The milky condition in this case was attributed to a fine dispersion of oil in the water. A test of the filter on such a dispersion was performed by dripping Jansolv directly into the feed pump suction screen. About 12.2 m/hr (5 gpm/sq ft) of 52 JTU, 12° C (54° F) water was treated with 21 wppm alum for the test. The rate of head loss was .088 m/hr (.29 ft/hr) with no Jansolv and .107 m/hr (.35 ft/hr) with 11 wppm of the dispersant. The difference between the average effluent turbidities was even less significant, going from 16 JTU with no dispersant to 17 JTU with it.

JAR TESTS

The bench scale screening tests of secondary flocculants were done with a gang stirrer. This device could be used to stir from two to six samples at the same speed simultaneously. The stirring speed could be varied from 15 to 100 rpm. Typically, four, 8-ml beakers of lagoon water would be stirred at about 20 rpm to simulate the movement of water in the filter, above the bed. Different flocculant-alum combinations were put into each sample and the floc formation was observed. The procedures were quantitative, but the results could only be expressed as "this is better than that" and were extremely subjective. The following conclusions were drawn from the jar test when no pH adjustments were made:

1. Alum and polymeric flocculant together treat Yorktown waste water better than either can alone.

2. Alum should be added before the polymer.

3. Cationic polymers work best for Yorktown waste water.

4. The turbulence produced by the filter feed water pump does not affect the treatability of the water.

5. A sample of water from a 7° C (45° F) lagoon does not respond to 30 wppm alum differently than the same water after it has been heated to 25° C (77° F).

The lack of observable temperature effect on chemical treatment response was somewhat different than observed for physical phenomena. Forty 2-hour quiescent tests indicated considerable temperature effect on settling. Samples of 53 JTU water settled after chemical treatment to yield a supernatent of 18 JTU at 40.5° C (105° F), 18 JTU at 24° C (75° F), 21 JTU at 13° C (56° F), and 27 at 4° C (39° F). Apparently, the increase in water viscosity at lower temperatures is sufficient to impede quiescent settling, but not clarification by flocculation in moving water.

MEDIA STERILIZATION

Although repeated sampling had indicated no media contamination or oil buildup problem, the condition of the support gravel was not certain. It seemed possible that a biological culture might have begun to grow on the support and that it could contribute detrimentally to the filter effluent. The unit was backwashed, shutdown, and allowed to stand full of a copper solution for 30 minutes in an attempt to loosen any biomass that might have accumulated. Sufficient copper sulfate was used to give 10 mg/l

copper in the water but the actual solution strength was somewhat less. Some of the ionic copper was reduced to elemental copper; it plated out on the metal dissolving apparatus and formed a colloid imparting a red-brown color to the water. No evidence of a biomass could be observed in the solution as it was drained. Time requirements for ingestion and toxication by copper are probably greater than 30 minutes, but it seems likely that copper was deposited in the unit to give a residual effect. No evidence of a biomass was ever seen and the unit performance did not improve after the treatment; however, it was performing excellently at the time and any improvement in performance would have been difficult to detect.

pH EFFECT

Yorktown lagoon effluent has exhibited extremes of pH from 6.0 to 8.9 during this study, but by far the majority of observations have been in the range of 6.8 to 7.5. The number of the pH observations that were considered above the range for good alum coagulation is listed below as a fraction of the total number of observations for the respective periods.

Quarter Ending	9-1-71	12-1-71	3-1-72	6-1-72	12-1-72
pH greater than 7.5	0/5	3/11	11/26	8/35	2/27
pH greater than 8.0	0/5	1/11	4/26	3/35	0/27

Repeated instances of high pH during early 1972 caused no decline in filter performance that could be attributed to pH alone. These high readings were the result of upstream conditions and practices (that have since been changed) and were always accompanied by high, filter inlet turbidities. Treatment effectiveness was not noticeably different from other periods of high turbidity at a pH range of 7 to 8.5. No facilities for pH adjustment were deemed justified.

CONTAMINANT LOAD, TEMPERATURES, AND THROUGHPUT EFFECTS

Correlations were developed between turbidity removal and incident turbidity, temperature, and throughput by plotting log sheet data. Scatter of these data was extreme but plotting median percent turbidity removal against 20 JTU increments of inlet turbidity, 2.8° C (5° F) increments of temperature or 11.4 cu m/hr (50 gpm) increments of throughput indicated the following linear relationships:

$R = 100 - 3.82\ (TP-7)$
$R = 1.14\ T + 0.8$
$R = 90 - 0.357\ I$

Where: R = percent turbidity removal
TP = hundreds of gpm throughput from 10 to 17.5
T = temperature from 4.5° C (40° F) to 29.5° C (85° F) expressed in degrees F.
I = incident turbidity from 10 to 140 JTU

These relationships were not intended to indicate unit capability, only to give a history of first-year, overall performance including operator error and equipment malfunction and to serve as a basis for evaluation of later improvements. The majority of high inlet turbidities occurred during the winter when the hydraulic load was the greatest and the water temperature the lowest, thus lending a bias to the data.

CHEMICAL TREATMENT TESTS

Definition of optimum chemical treatment for any specific waste water certainly would have only limited applicability. Simple chemical pretreatment using primary coagulants likewise has only limited applicability to most waste waters since it typically results in a "scalping" operation that does not achieve essentially complete removal of suspended material by filtration. Optimum chemical pretreatment to achieve consistent near-potable, water clarity usually requires more response to water chemistry than just the use of primary coagulants. This aspect of pretreatment is discussed in a later section comparing results at other refineries to results at Yorktown.

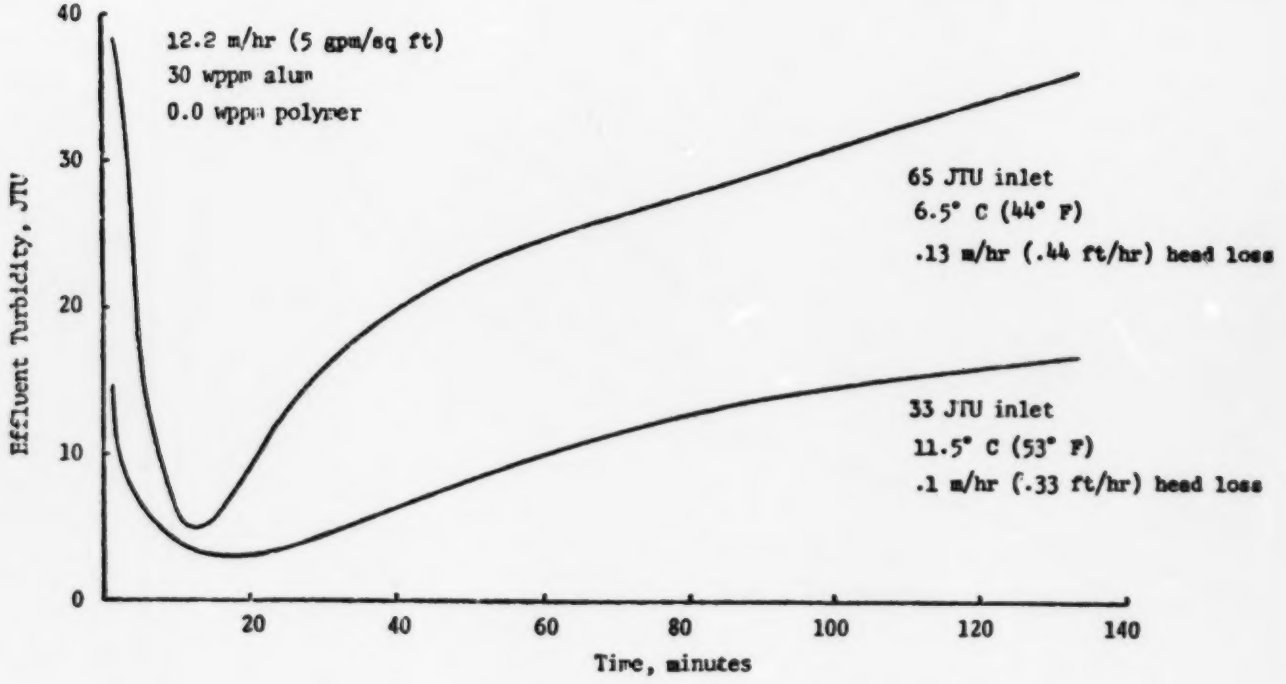
The results of Yorktown's preliminary treatment tests are shown in Table 3 and Figures 14 through 20 only to indicate basic equipment responses. The date of each test has been coded into a test number using one digit for the year, two for the month, two for the day, and one for the test number. Each test was begun after a normal backwash during which the polymer addition rate was confirmed at the injection point. The filter-effluent turbidity and pressure were recorded as the only criteria for a successful chemical treatment. The head loss rate after the first 20 minutes was essentially constant for the 2 1/2-to-3-hour tests. In this open top unit, a decrease in pressure (head loss) at the effluent is equivalent to an increase in differential pressure as often reported in the literature. Effluent turbidity did not remain constant or increase at a constant rate during most normal operations. An arithmetic average of the turbidity at 20, 50, and 120 minutes after the test started was arbitrarily chosen to represent the effluent turbidity as a single number. The polymeric flocculant in use at the time was Betz 1175.

The effects of contaminant load and temperature on effluent quality are deomonstrated in Figure 14. Polymer addition at a constant alum dosage improved effluent quality as shown in Figure 15.

Table 3. YORKTOWN WATER FILTER CHEMICAL TREATMENT TEST DATA

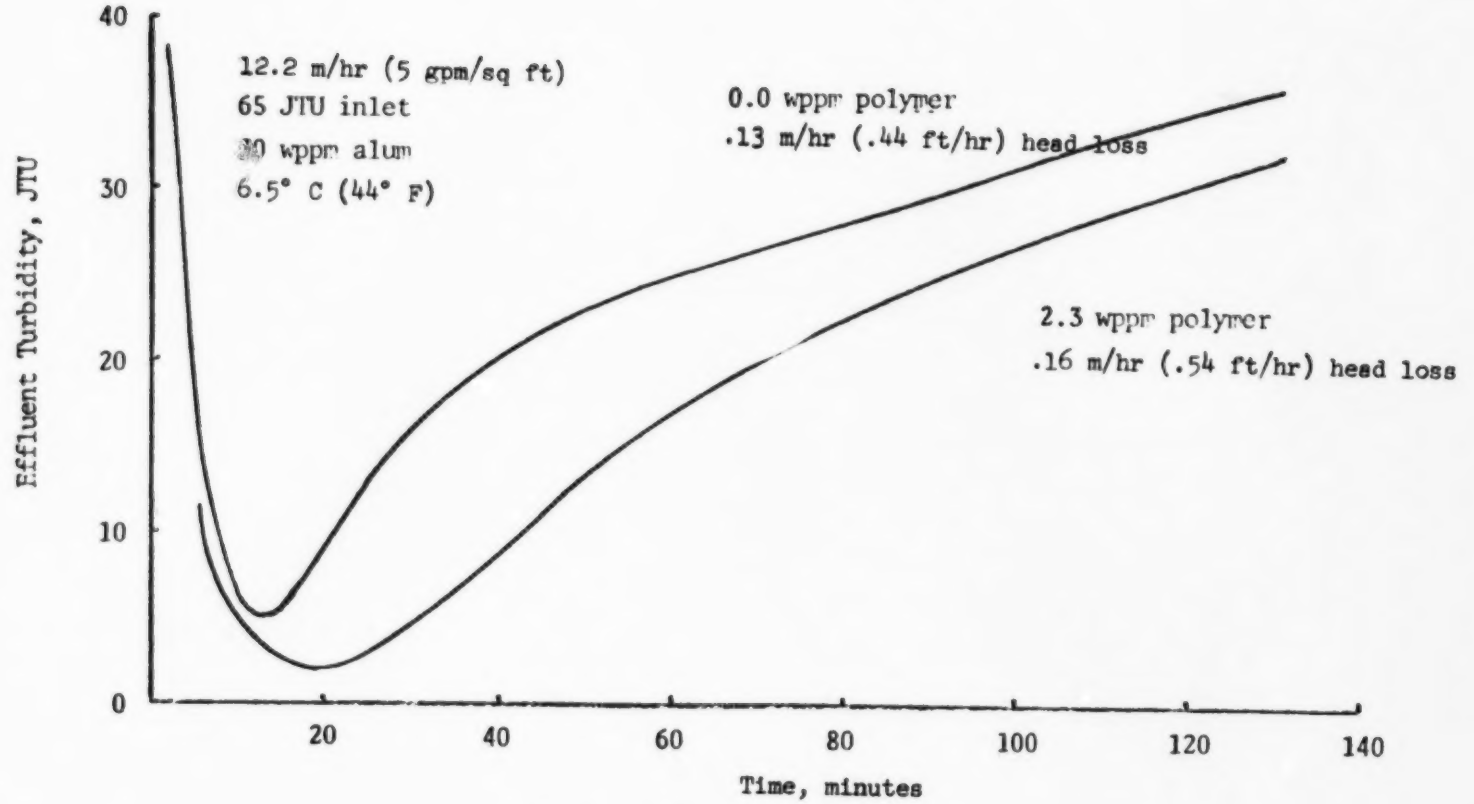
Test #	Water rate, m/hr	gpm/sq ft	JTU Inlet	JTU Outlet	Temp. °C	Temp. (°F)	Alum wppm	Polymer wppm	Head loss, m(ft)	Head loss, H_2O/hr
201121	12.2	(5.0)	55	11	14.5	(58)	30	0.0	.18	(0.60)
201122	12.2	(5.0)	55	14	14.5	(58)	33	0.0	.12	(0.38)
202081	12.2	(5.0)	80	18	5.5	(42)	45	3.2	.23	(0.74)
202091	12.2	(5.0)	65	22	6.5	(44)	30	0.0	.13	(0.44)
202091	12.2	(5.0)	65	15	6.5	(44)	30	2.3	.16	(0.54)
202101	12.2	(5.0)	54	9	5.5	(42)	15	1.0	.12	(0.39)
202111	12.2	(5.0)	48	9	6	(43)	7.5	1.1	.08	(0.27)
202251	12.2	(5.0)	52	15	10	(50)	22	0.34	.1	(0.33)
202291	12.2	(5.0)	33	9	11.5	(53)	30	0.0	.1	(0.34)
203011	12.2	(5.0)	28	6	13	(55)	30	*	.16	(0.51)
203071	12.2	(5.0)	80	21	11.5	(53)	9	1.9	.11	(0.36)
203281	12.2	(5.0)	52	16	11	(52)	21	0.0	.09	(0.29)
203282	12.2	(5.0)	52	17	13.5	(56)	21	0.0	.11	(0.35)
204051	12.2	(5.0)	170	110	13.5	(56)	27	0.0	.04	(0.13)
204062	12.2	(5.0)	155	110	13.5	(56)	3.8	5.0	.003	(0.01)
204063	12.2	(5.0)	155	39	13.5	(56)	27	5.0	.06	(0.19)
204064	12.2	(5.0)	155	48	13.5	(56)	27	11.8	.09	(0.29)
205301	6.5	(2.67)	100	17	23	(73)	52	0.0	.13	(0.44)
206011	7.3	(3.0)	50	12	21.5	(71)	10	5.3	.07	(0.23)
206012	9.8	(4.0)	63	21	22	(72)	10	0.27	.08	(0.26)
206021	13.7	(5.60)	51	25	21.5	(71)	10.4	0.20	.12	(0.39)
206022	6.5	(2.67)	50	17	23	(73)	9.8	0.40	.05	(0.16)
206031	6.5	(2.67)	44	4	22	(72)	22.2	0.40	.07	(0.24)
206032	9.8	(4.0)	43	11	23	(73)	14.9	0.36	.12	(0.38)
305021	12.2	(5.0)	22	3	-	-	28	0.0	.43	(1.42)
305031	12.6	(5.17)	16	2	-	-	27	0.0	.54	(1.76)
306141	13	(5.33)	23	6	29	(84)	20	0.0	.32	(1.05)

NOTES: Test no. 203022 followed the injection of polymer in the backwash.
Test no. 203282 water contained 11 wppm oil dispersant.
Tests no. 30502, 30503, and 30614 were with the replacement bed.



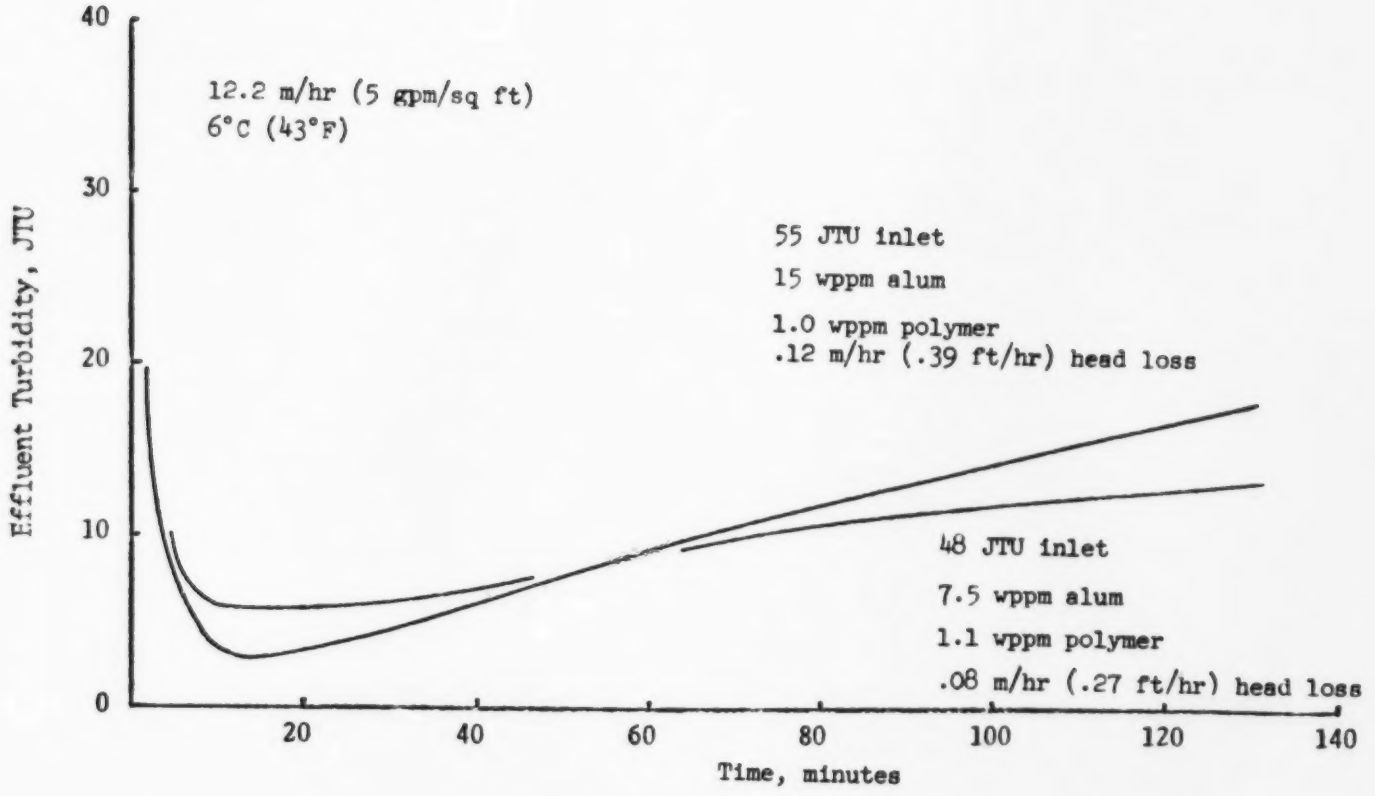
Yorktown filter chemical treatment tests

Figure 14



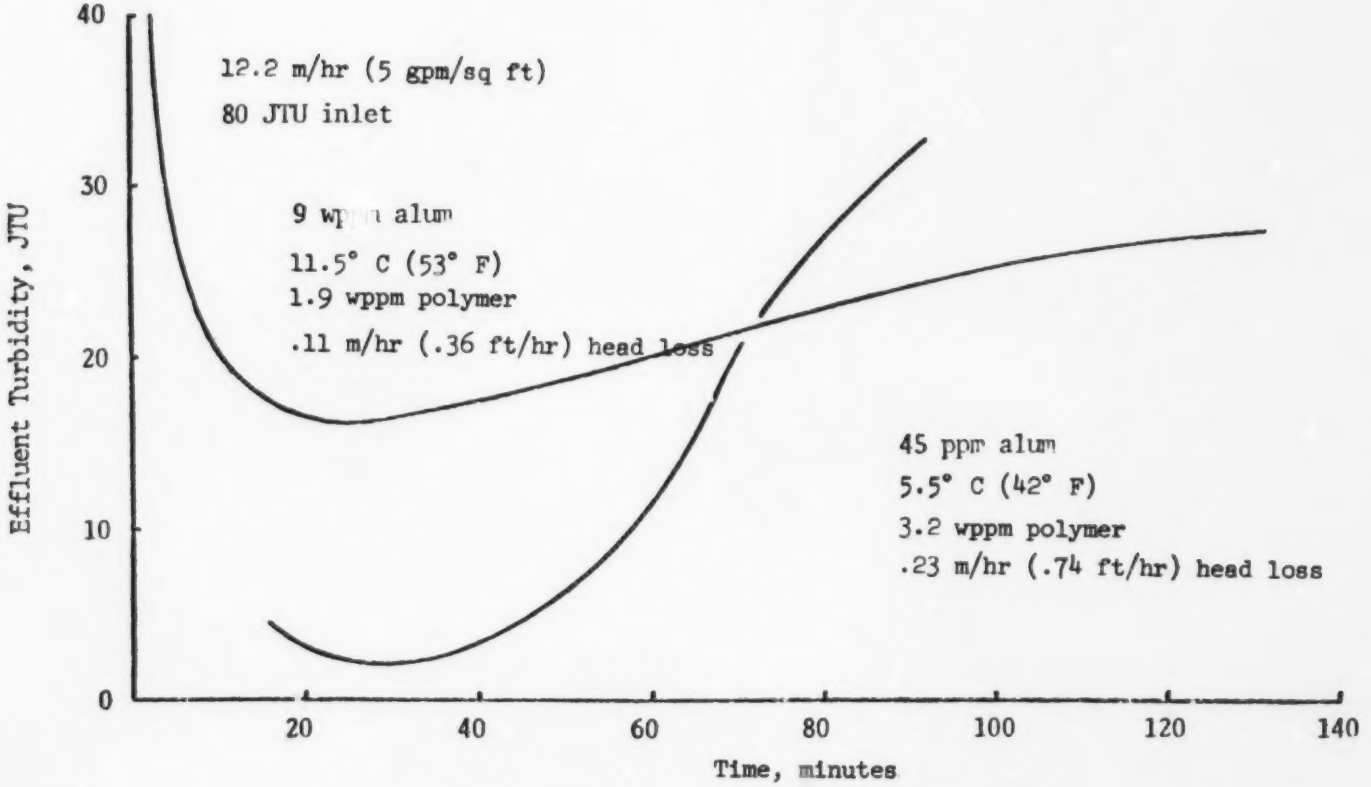
Yorktown filter chemical treatment tests

Figure 15



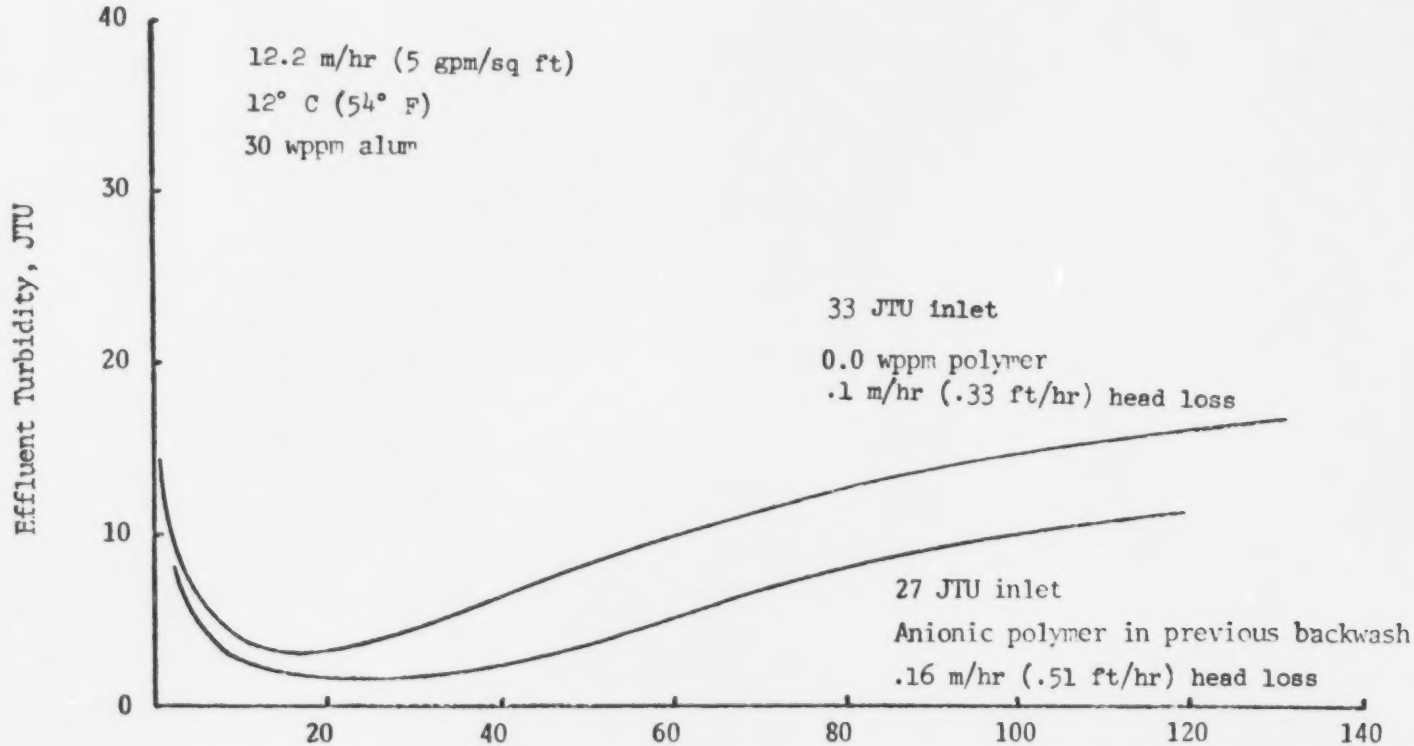
Yorktown filter chemical treatment tests

Figure 16



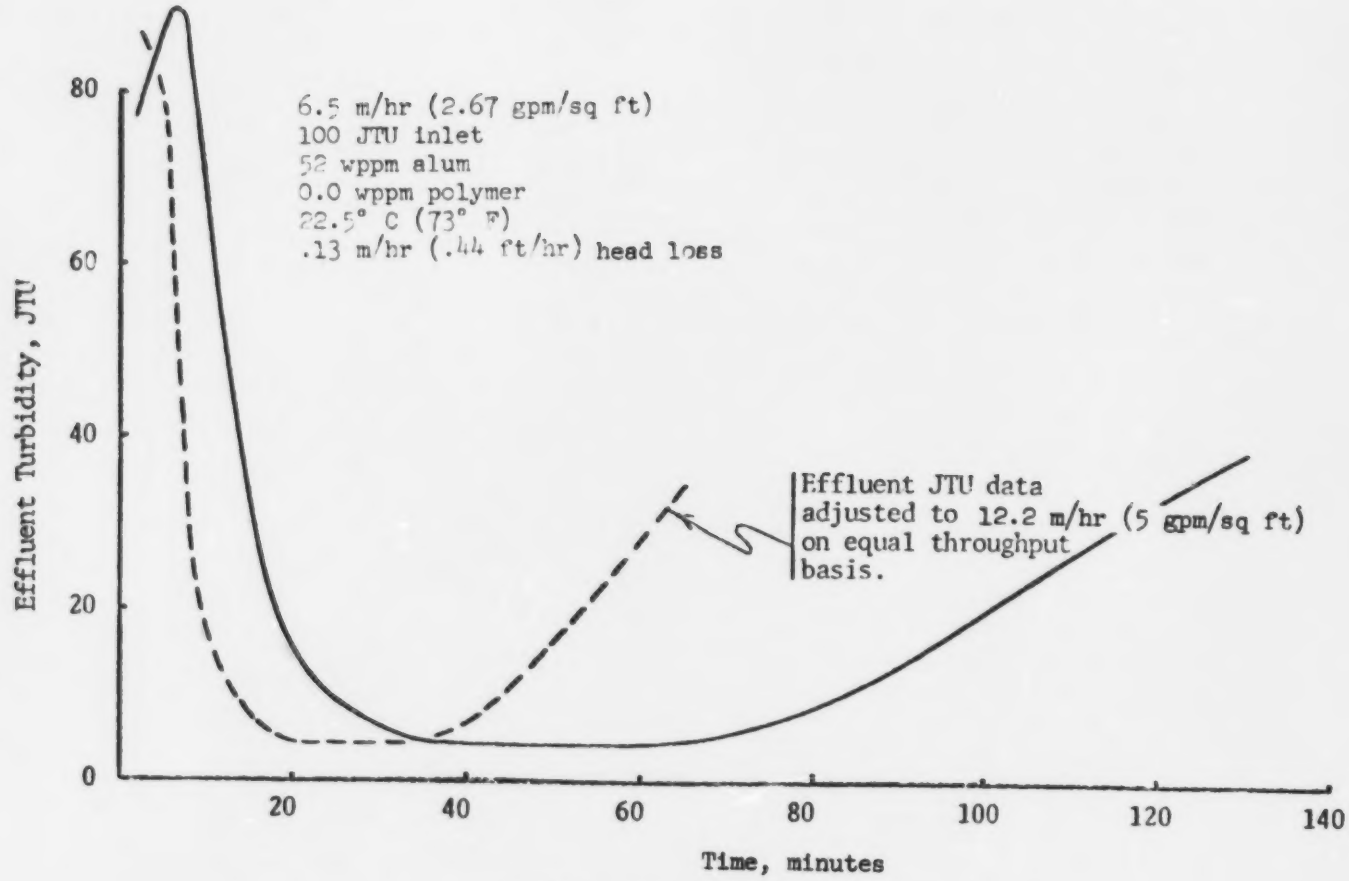
Yorktown filter chemical treatment tests

Figure 17



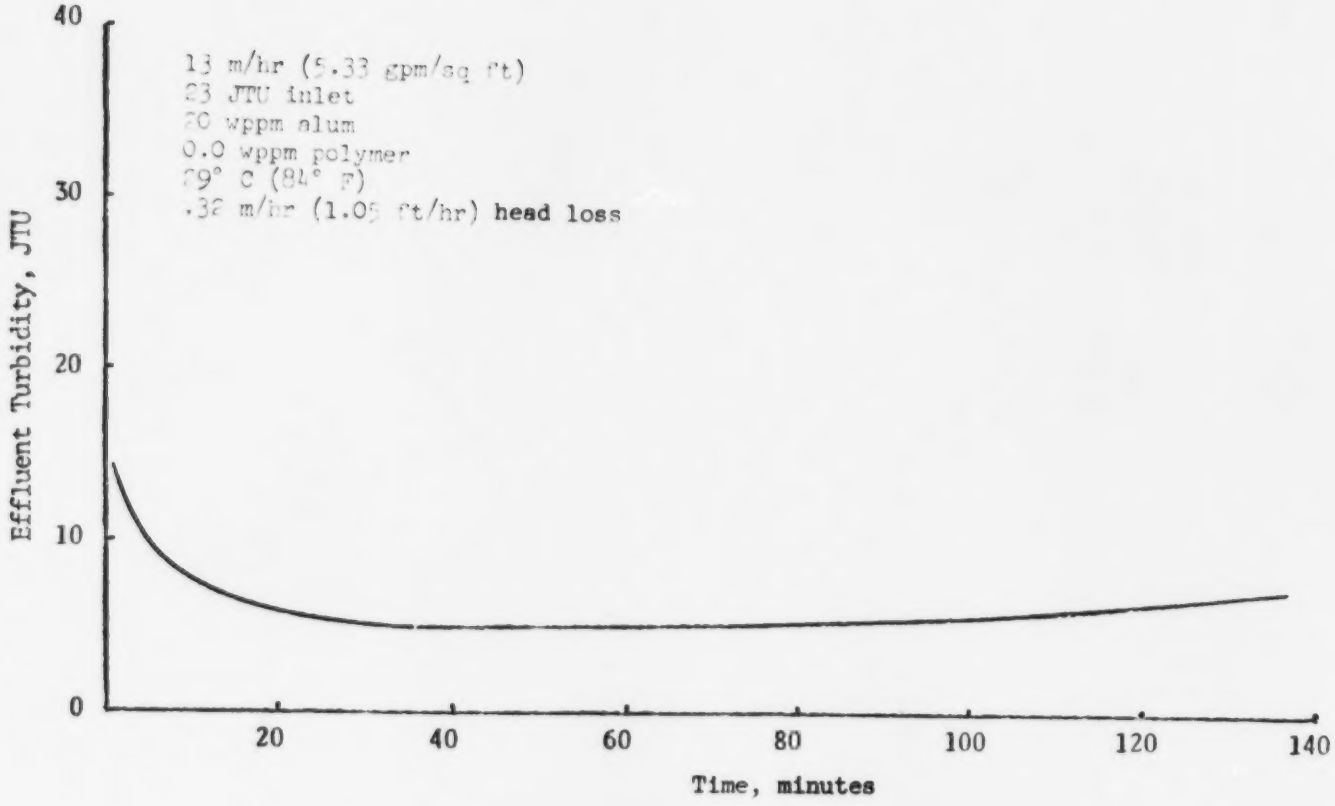
Yorktown filter chemical treatment tests

Figure 18



Yorktown filter chemical treatment tests

Figure 19



Yorktown filter chemical treatment tests

Figure 20

Additional effluent improvement could usually be demonstrated by reducing the alum feed when a secondary flocculant was being used. Figure 16 is an indication of the response to 1/2 and 1/4 the alum dosage reported for Figure 15 with about the same and double the polymer alum ratio. Even after recognizing that the effluent should be better with a lower influent turbidity, it still appears that the lower treatment levels produced a better effluent and a lower head loss rate. One result of over-treatment can be seen in Figure 17. The relatively low minimum turbidity, high head-loss rate, and poor sustained performance all indicate that the filter was filling up with unnecessary chemical floc. Figure 18 was developed from a test using a high molecular weight, weakly anionic polymer in the backwash in an attempt to "make the bed sticky". Forty-five grams of solid were dissolved and injected into the backwash line during a 90-second upflow, following a normal backwash. The increased head-loss rate and the improvement in the effluent quality indicate some success with the technique. This "flypaper type" entrapment is not the normal use of filter media and there is considerable doubt that backwashing would be effective after prolonged use of this technique.

The curves in Figure 19 represent data from a test run at 6.53 m/hr (2.67 gpm/sq ft) with the solid line plotted as run. The dashed line represents the same effluent turbidity versus cumulative throughput data, but as plotted as if it had been run at 12.2 m/hr (5.0 gpm/sq ft). The similarity between the dashed line of Figure 19 and the high alum curve in Figure 17 suggests that throughput rate is not the predominant independent variable. Head loss, when similarly adjusted from 6.5 to 12.2 m/hr, was .25 m/hr (0.82 ft/hr) for the dashed line. In other words, contaminant removal from a given quantity of water is nearly independent of the filtering rate between 6.53 and 12.2 m/hr.

Test data from the replacement bed are represented in Figure 20. This curve most nearly corresponds to test 202291 (the upper curve in Figure 18), but the 40-percent lower-inlet turbidity during the later test makes the magnitude of the improvement associated with the new bed questionable. One of the stated purposes of the newly-designed bed, no increase in head-loss rate, was not achieved. For a comparable 75-percent contaminant removal, the new bed had three times the head-loss rate of the damaged bed and twice that demonstrated in the pilot unit.

SECTION VIII

PROJECT CRITIQUE

AESTHETICS

The Yorktown mixed media filter has been a valuable addition to the refinery waste water treatment system. It has removed more contaminants from the water than expected and has exhibited considerable public relations appeal. Visitors have been impressed with the visible differences between the influent and effluent water and with the contaminant removal evidenced by waste water flowing from the troughs into the gullet during a backwash. The only disappointment associated with the project has been the effluent turbidity level. An average of less than three had been expected using only primary coagulants. Longer term operating experience demonstrated that the brackish water biocolloid system requires a more sophisticated chemical treatment than simple primary coagulants, and further definition to this will be given during the 1973-1974 winter, the most demanding season. Information on hydraulic and contaminant loads that was collected to provide a design basis for the unit was accurate, but quite inadequate. No consideration was given to possible differences between summer and winter lagoon operation that might change the filter influent conditions. Before startup of the plant filter, a number of decisions were made that changed the properties of the water to be filtered. For example, a change in company policy to prevent partial deballasting of product tankers at sea caused an unanticipated increase in throughput requirement, contaminant loading and salinity. A second decision impacting on filter operations involved backwashing the filter to the second cell of the four cell lagoon. The objective of this operation was to eliminate the substantial cost of a backwash surge pond and desludging pit. However, this operation resulted in recycling solids to the filter thereby increasing the solids burden, and seems to have contributed to more pronounced spring and fall turnovers which also increased the loading on the filter. Subsequent to this experience, a backwash sludge pit has been added to the system to effect removal of backwash solids from the system.

Several years experience has shown that the Yorktown refinery lagoon effluent lends itself to filtration without causing media contamination problems. Traces of oil do not accumulate in the bed and no mud balls were formed at the chemical dosages used during this project.

PROCESS LIMITATIONS

Pump sizes limit the unit throughput and treatment dosage to about 397 cu m/hr (1750 gpm) and 25 wppm alum. No permanent secondary flocculant pump has yet been installed. Given the above constraints, the minimum effluent turbidity is limited to some unknown extent by the untreated lagoon water left in the unit after a backwash. Over compensation for this effect might cause an alum over-treatment and shortened run lengths. Run lengths are determined by the head loss rate, which is a function of incident turbidity and chemical treatment. The backwash switch has usually been set to terminate a run after .6 to 1.2 m (2 to 4 ft) of water total head loss. Run length then automatically shortens if the influent turbidity rises.

FILTERED WATER FOR BACKWASH

Consideration has been given to adding filtered water storage and a pump to allow backwashing with cleaner water. Present unit capacity makes this nearly impossible since only 160 minutes of filtering time are presently available in a 3-hour cycle. The influent pump is down for 9 minutes and 11 minutes are required to fill the unit after a backwash. Therefore, the influent rate must be 386 cu m/hr (1,700 gpm) to average 343 cu m/hr (1,510 gpm) for an extended period such as the last project quarter. The summertime backwash rate is about 1363 cu m/hr (6,000 gpm) and with a minimum acceptable duration of five minutes the reprocessing load would be 113.6 cu m (30,000 gallons). A rate 429 cu m/hr (1,890 gpm) would be required to maintain the same 343 cu m/hr (1,510 gpm) average. This is above the feed pump capacity and in an untested region as far as filter efficiency is concerned.

SECTION IX

THEORY AND PRACTICAL APPLICATION OF CHEMICAL PRETREATMENT

FILTRATION REQUIRES DESTABILIZATION OF COLLOIDS

Refinery waste water suspensions that are the target of filtration applications usually are essentially all colloidal or a combination of colloidal and very slightly flocculated suspensions. Work at other Amoco refineries indicates that the optimal application of filtration to these waters relates primarily to recognizing and responding to the required water chemistry for destabilizing the colloidal material and only secondarily to the design of the filter.

Mechanisms for retention of solids within the pores of filter media may be separated into two principal processes: a transport step and an attachment step. The transport step involves movement of the dispersed phase material to the vicinity of the filter media surface, and the attachment step involves attachment of the particles on the media surface. The transport mechanisms may involve diffusion, interception, sedimentation and hydrodynamic actions. The attachment mechanisms may involve van der Waal forces, electrical double layer interaction, mutual adsorption or hydrogen bonding (1). Experimental comparisons of the filtration of colloidal, ferric hydroxide suspensions with the filtration of well flocculated suspensions of ferric hydroxide, both performed under identical conditions of filtration, demonstrate a much higher filtration efficiency for the floc. Studies (2) have shown that removal of colloidal suspensions by filtration appears to be possible only when the colloidal particles to be filtered carry an electro-kinetic charge opposite to the charge of the filter media used. The removal of the colloid is by electro-kinetic sorption of the colloidal particles on the surface of the filter media. This kind of "filtration" phenomena seems to have limited application to the filtration of industrial waste water because of complications encountered in application, the complexity of which are beyond the scope of this report.

For example, however, at a high ratio of the amount of colloidal particles to the amount of filter media, the filter media soon accepts the surface charge of the colloidal particles as a result of sorption of them and the charge of the colloidal particles does not change appreciably. As a result sorption ceases. If, in contrast, the amount of colloidal material is small in proportion to the amount of filter material, the colloid is removed rapidly initially but ceases when the media changes charge due to sorption.

A dilution or filtration effect (sorption/desorption of "soluble" surface ionic species) may cause the charge of the remaining colloids in suspension to change and sorption is again initiated until sorption changes the charge on the media once again. Thus, by this mechanism erratic performance may ensue.

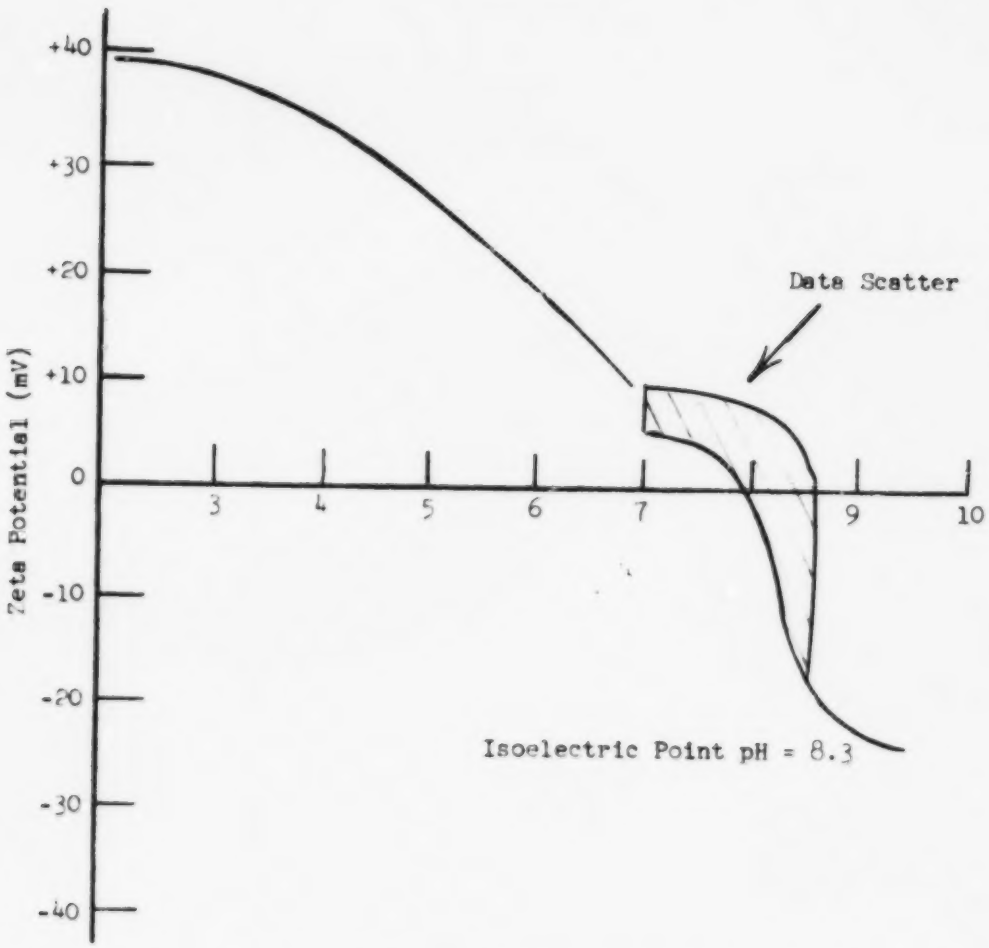
COLLOIDAL DESTABILIZATION

In most cases, the application of filtration to industrial waste waters will not be optimized unless the colloidal material in suspension is destabilized by essentially neutralizing the surface charge on the colloids. The surface charges (measured as zeta potential) of suspended matter in refinery process water effluents have been found to range from -35 to -55 mV. The neutralization of the charge using conventional primary coagulants is simple, but must recognize the condition of the water. Overdosing with alum, for example, can be a most deleterious response to make to a direct filtration system that is not performing satisfactorily.

Destabilization of colloidal suspensions using salts of iron and aluminum as primary coagulants must recognize the properties of these primary coagulants. In Figure 21 the zeta potential of colloidal iron hydroxide solutions is plotted as a function of pH. The zeta potential decreases in positive charge as the pH increases until the isoelectric point is reached at a pH of 8.3 at which the charge reverses. In the vicinity of the isoelectric point, the charge may vary as indicated. Alum has similar zeta potential-pH relationships as shown in Figure 22. The zeta potential may be negative or positive over the pH range of 7.0 to 7.8.

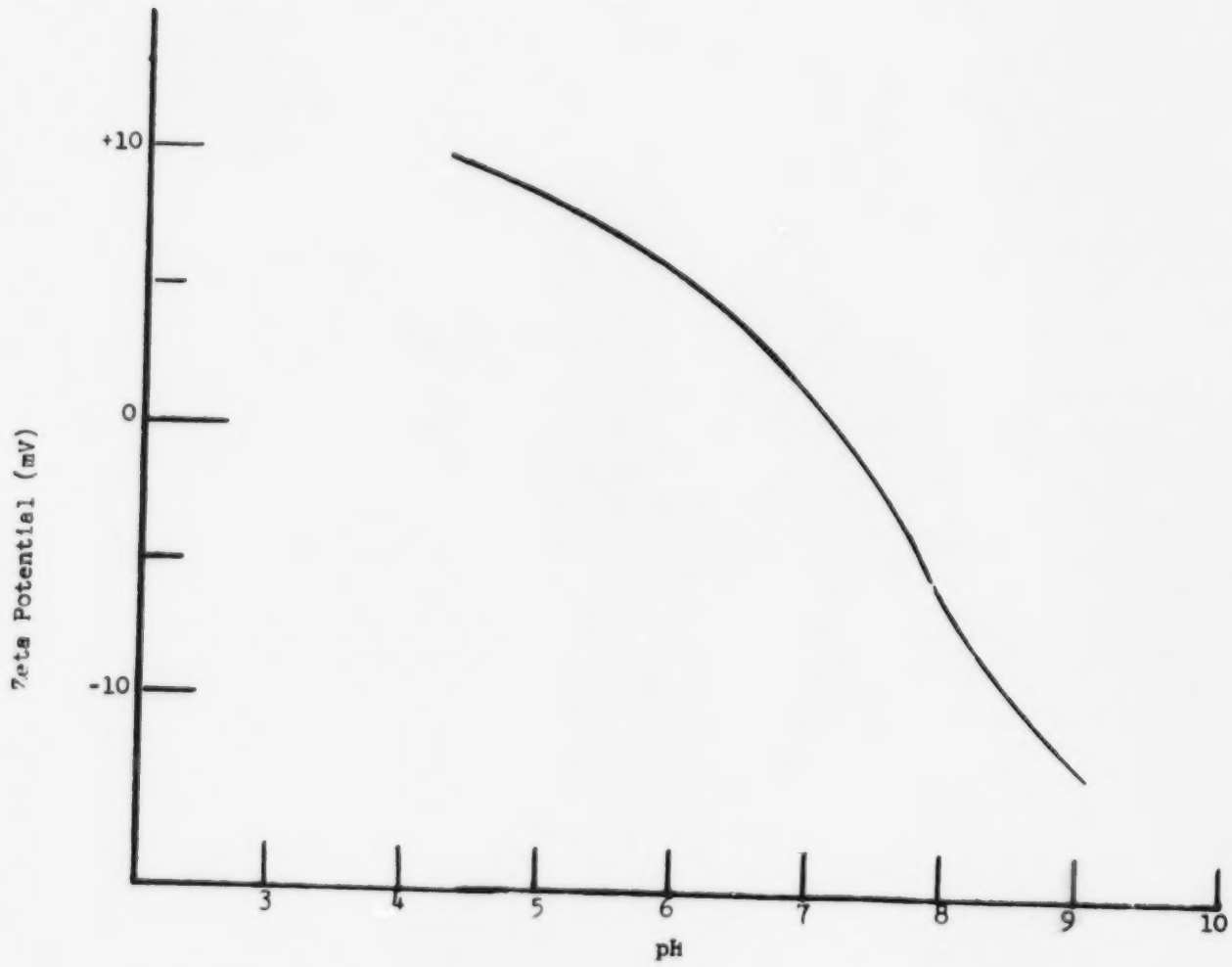
The amphoteric property of alum shown in Figure 23 is an additional factor that must be considered. Other properties of water bear importantly on alum solubility in alkaline solutions that may sharply limit the operable pH range.

Stumm and O'Melia (3) describe the equilibrium composition of solutions in contact with precipitated primary coagulants in the interesting manner shown in Figures 24 and 25. These diagrams are calculated using equilibrium constants for solubility and hydrolysis equilibria. The shaded areas A and B in each figure are approximate operation regions for air flotation and clarifiers (region A) and direct filtration (region B). Both regions are assumed to cover a pH range of 6.0 to 8.5. The coagulant dosage ranges from 33 to 200 mg/l in region A and 3.3 to 20 mg/l in region B. These figures are useful in the interpretation of some of our filtration results.



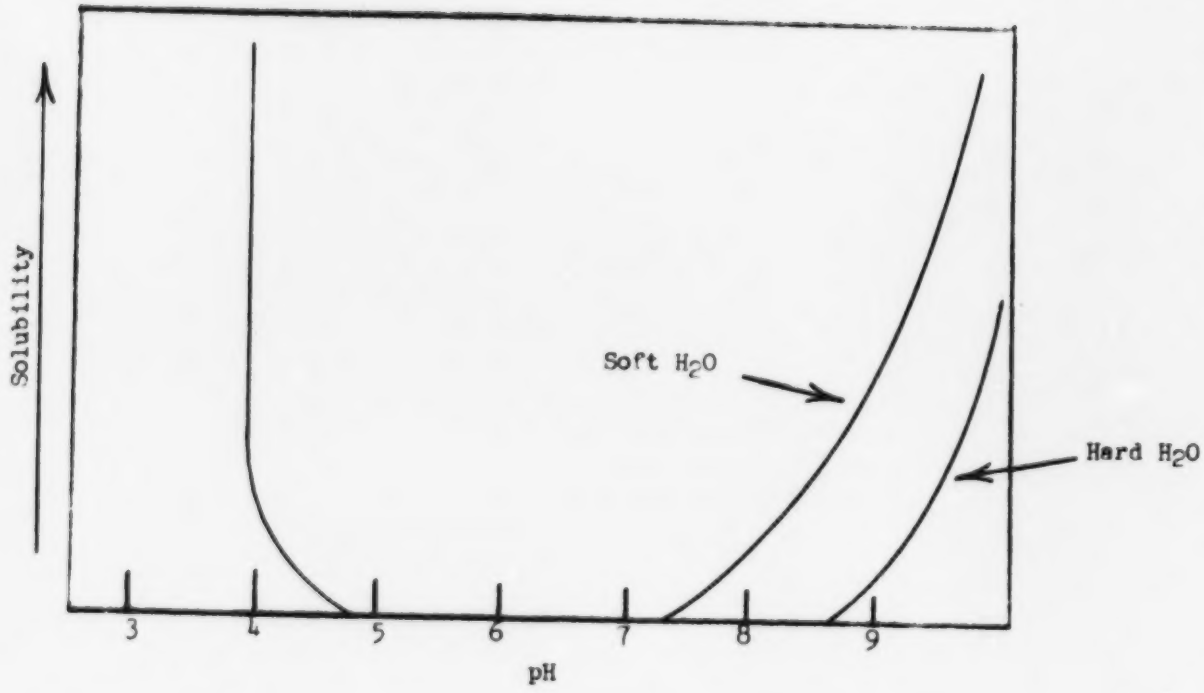
Zeta potential of colloidal iron hydroxide solution plotted as a function of pH

Figure 21



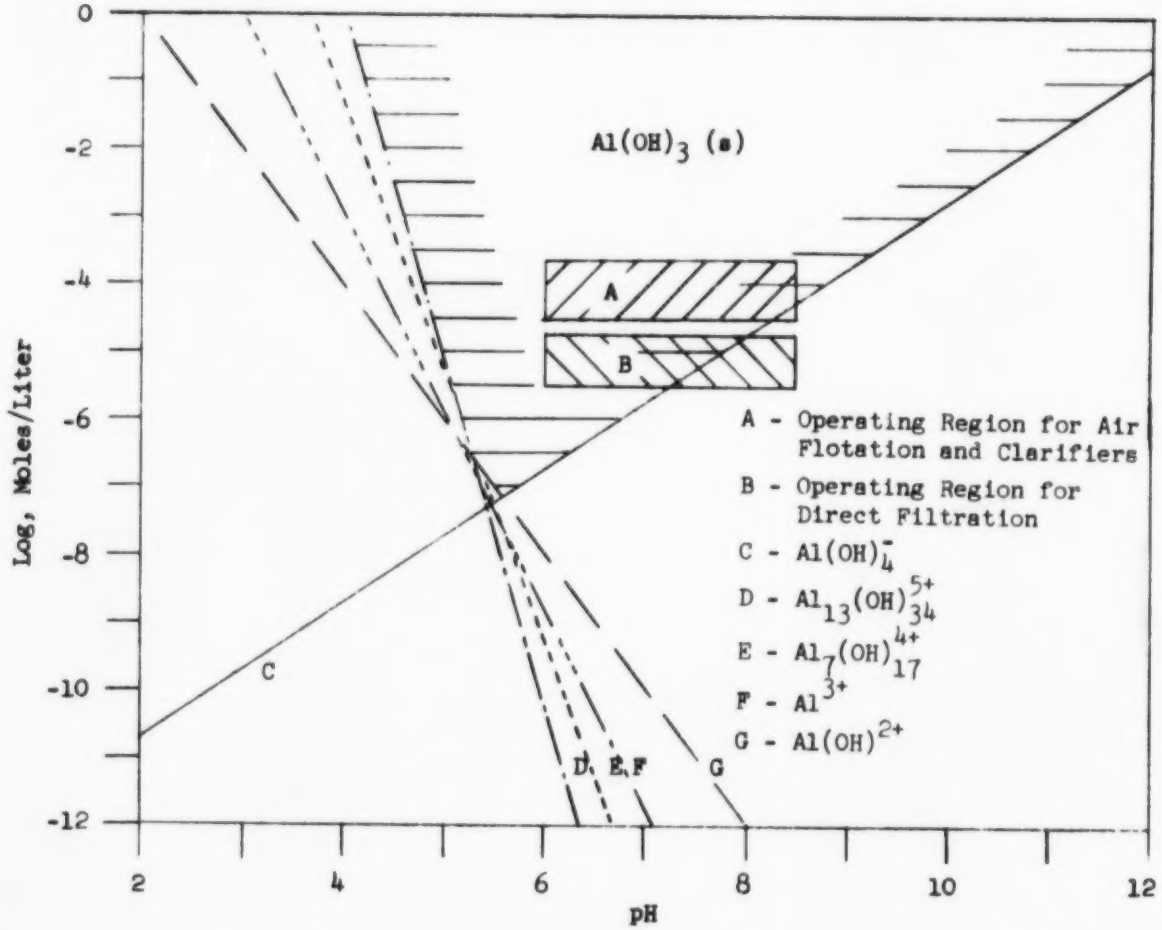
Zeta potential - pH plot for aluminum hydroxide

Figure 22



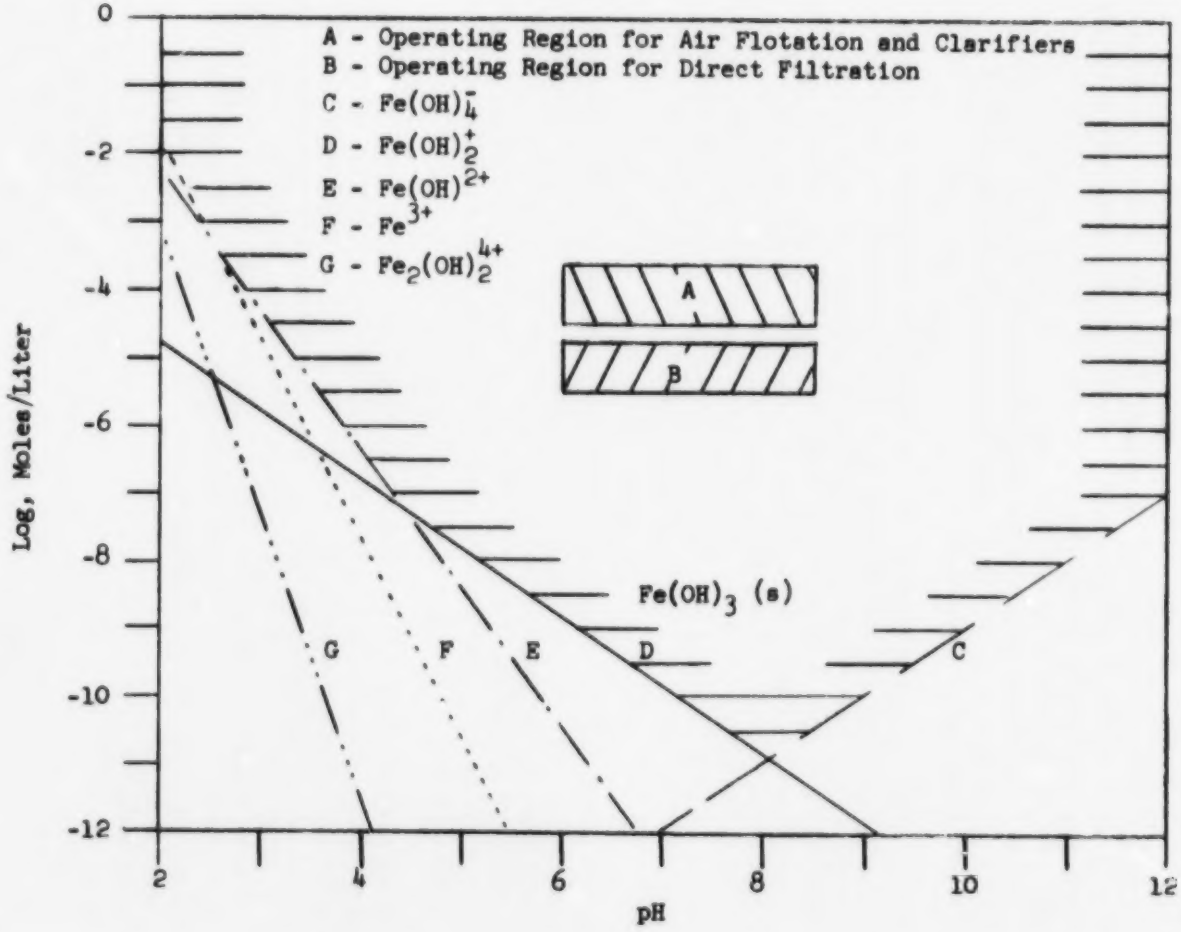
Solubility curve for aluminum

Figure 23



Equilibrium compositions of solutions in contact with $Al(OH)_3$

Figure 24



Equilibrium compositions of solutions in contact with $Fe(OH)_3$

Figure 25

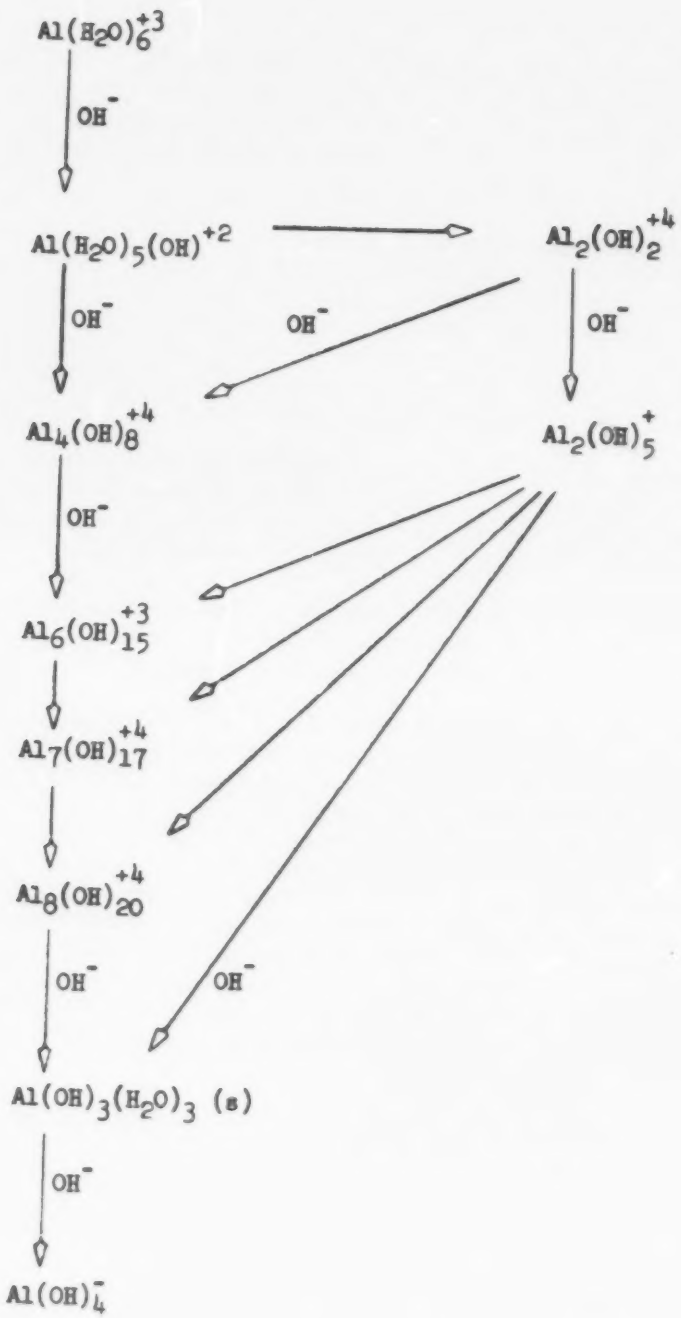
With reference to Figure 25, the isoelectric point for ferric hydroxide coincides with the region of minimum solubility, and the operating regions for water treating (destabilization) always yield a hydrolyzed primary coagulant with a desirable, positive, zeta potential.

In many refinery situations, however, it is difficult to use this desirable condition because the presence of sulfides and strongly reducing conditions cause the reduction of ferric to ferrous iron and the formation of mixed iron sulfides with no coagulation powers. In fact, in some refinery waters the use of iron coagulants at modest dosages may contribute to stabilizing solids rather than destabilizing them.

While alum has no redox or sulfide chemistry comparable to iron, its amphoterism and solubility pose definite limitations on alum usage. With reference to Figure 24, a substantial portion of operating region B lies in the area where alum is soluble and the predominant equilibrium species is negative, $Al(OH)_4$. In the more acidic part of region B, however, the concentration of equilibrium ionic species is very much lower and much less negative. Considering these data, it is not unexpected that investigators consistently report optimal coagulation/flocculation results with alum at a pH of 5-6.

With inspection of Figure 24, one may question why alum is effective at all for neutralizing negatively charged colloids in the indicated operating regions. One approach to explaining observed performance requires understanding that the data in Figure 24 are equilibrium data; but before equilibrium is reached, substantially different conditions exist.

Alum very readily hydrolyzes to form polymers in a complex manner not well defined. The hydrolytic pathway and reaction rates are affected by pH, temperature, other ions, etc. One hypothesized route which includes different aluminum hydrolysis products known to exist is outlined in Figure 26. When alum is added to water in amounts which exceed the solubility limits, sequential kinetic reactions occur until the ultimate precipitate is formed and the ionic species appropriate to the pH equilibrate with the precipitate. The hydrolytic reactions are not instantaneous, and as they proceed, positively charged hydroxo polymers are formed which are available for colloid adsorption. The hydrolyzed species have enhanced adsorption capabilities possibly due to larger size, less hydration, and the presence of coordinated hydroxide groups (3). In solutions more alkaline than the isoelectric point, the positively charged polymers are transient and, at equilibrium, anionic polymers prevail. In modestly alkaline solutions, the transient,



Conversion of $Al(H_2O)_6^{+3}$ to $Al(OH)_4^-$

Figure 26

positively charged polymers appear to contribute to destabilization of colloids. On the other hand, in solutions more acidic than the isoelectric point, the positively charged polymers prevail at equilibrium and destabilization of colloids is achieved at significantly lower coagulant treatment levels.

While coagulation/flocculation of refinery waste water can frequently be achieved over a wide pH range using primary coagulants supplemented with polyelectrolytes, typically there is a very definite optimal pH that may simplify, or even be required by, direct filtration. Operating at the optimal pH yields benefits of maximum removal of discontinuous phase material with minimal coagulant requirement and sludge generation.

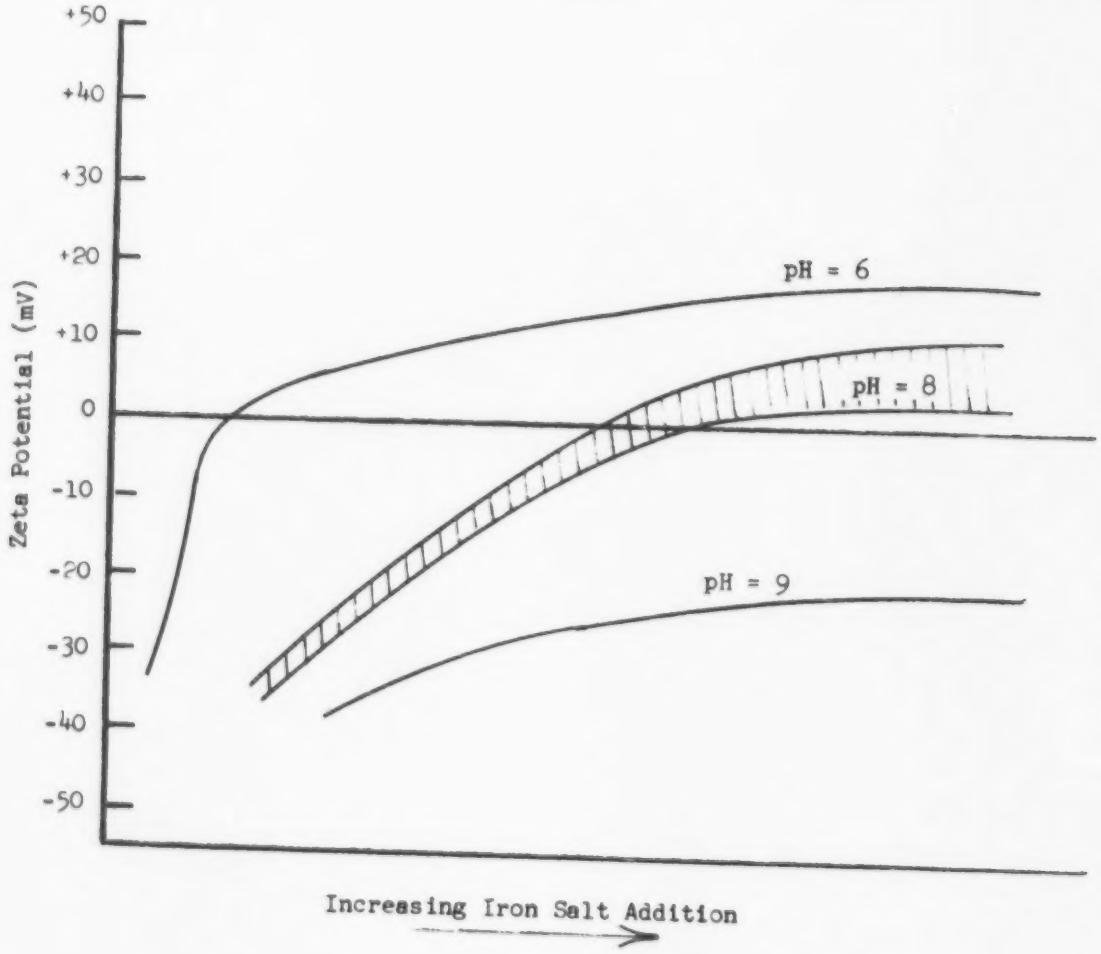
In Figure 21 (page 51), the zeta potential-pH relationship is shown for a primary coagulant. The use of this primary coagulant to treat a refinery process water containing negatively charged colloids is shown in Figure 27 at three pH levels.

At a pH of 6, a minimal dosage of coagulant rapidly changes the zeta potential of solids in the system to zero thereby destabilizing the suspension adequately for direct filtration.

Frequently, refinery waste waters only require 5 to 10 mg/l of primary coagulant in this pH range to achieve destabilization for filtration. When this level of chemical treatment is observed in jar tests, the coagulant dosage may be much below that required for generation of floc; however, excellent filtration results are achieved. The destabilized particles penetrate into the pores of the filter media, the media aids the flocculation process, and the particles are effectively trapped with high solids loadings. Too much primary coagulant can be added at a pH of 6 and some suspended matter restabilized. To much coagulant puts an unnecessarily heavy solids burden on the filter and the result is rapidly increasing pressure drops, early breakthrough and excess backwash sludge to handle.

At a pH of 8, substantially more primary coagulant may be needed to neutralize the zeta potential. The dosage may be 30 mg/l or more with the generation of a substantial floc size instead of the almost invisible pin-point floc of suspensions successfully filtered at a pH of 6. The more voluminous floc does not penetrate into the filter media as well as does the pin-point floc and lower solids loading, higher pressure drops, and more chemical usage, backwash and sludge volumes result.

At a pH of 9, the zeta potential of the system may never be neutralized and, of course, is not optimal as such for direct filtration. With iron salts, chemical coagulation/flocculation at a



Change in zeta potential of refinery process water with increasing coagulant dosage at various pH levels

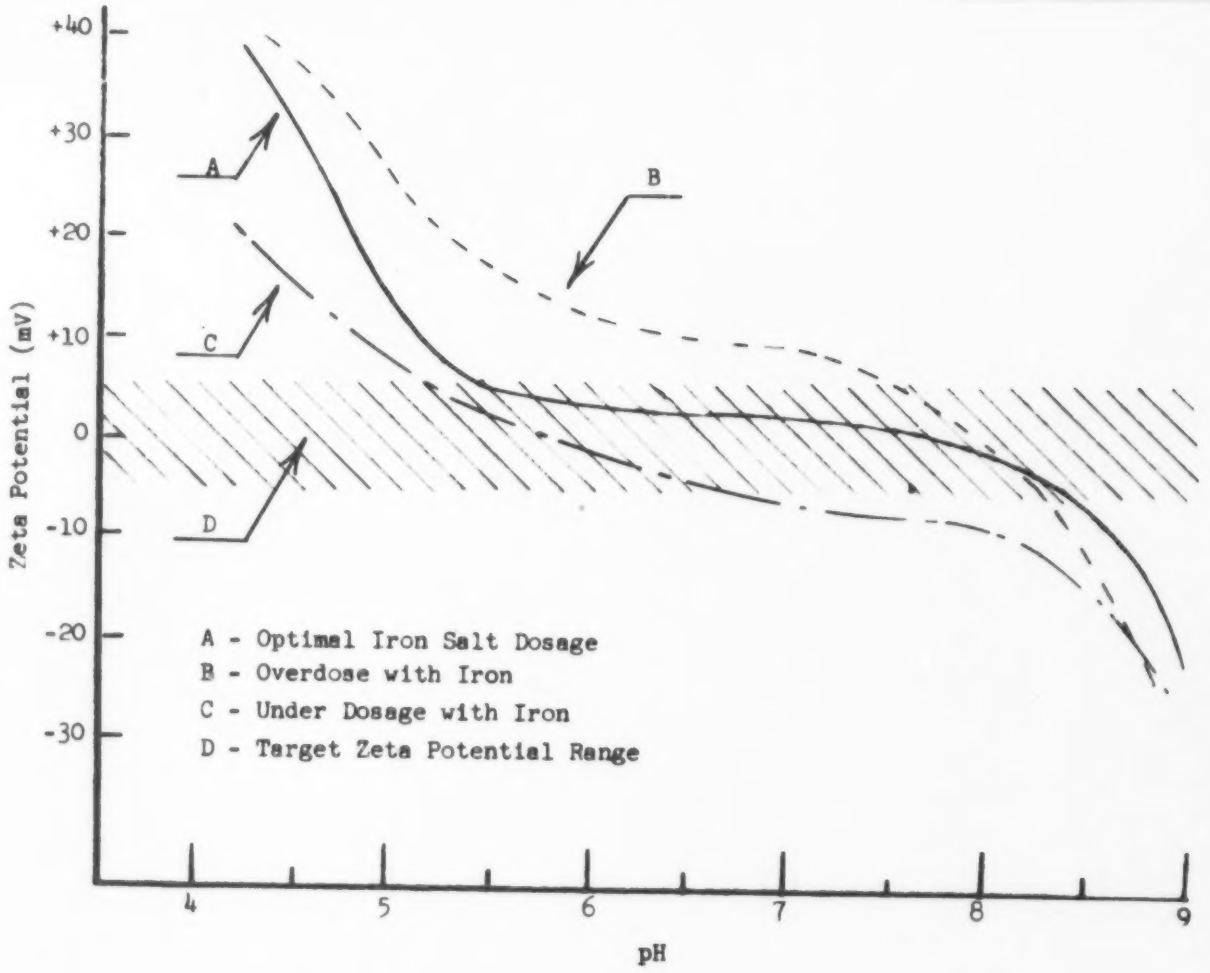
Figure 27

pH of 9 or more can yield superb results with some waters, but a different clarification mechanism is involved. Comparatively large dosages of coagulant are used which generate large, voluminous floc particles that trap and enmesh the suspended matter in the water being treated and retain the solids in the sludge blanket. This approach is not optimal for direct filtration but requires pretreatment in a clarifier to handle the voluminous sludge volume generated. The clarified water is then polished by filtration using polyelectrolytes to destabilize the residual suspended matter.

Figure 28 illustrates the effect of treating a refinery effluent water with fixed levels of overdosage, underdosage, and optimal dosage of primary coagulant at various pH levels. For this example, the optimal dosage is defined as the coagulant required to bring the zeta potential of the system into the target zeta potential range of $\pm$ 5 mV necessary for destabilization of the suspended matter preparatory to direct filtration. To emphasize the importance of pH for these systems of over, under, and optimal treating with coagulant, there is a pH range where the system is destabilized and receptive to clarification by direct filtration.

For the optimal dosage in curve A, the system is destabilized over the widest pH range of 5.5 to 8.4. Underdosing (curve C) provides a destabilized system for filtration only at a pH of about 6.5 or less. Overdosing (curve B) results in the narrowest pH range for effective destabilization of about 0.6 pH units, i.e., 7.65 to 8.25.

Industrial effluent waters may vary rapidly in pH over a short time span which makes it desirable to determine the optimal coagulant-pH balance. Frequently, poor or no pH control is available. In these cases, the destabilization of suspended matter frequently can be "desensitized" to pH somewhat by using coagulant/polyelectrolyte combinations. The preferred operating procedure that frequently makes the filtration system essentially free from upset is a two chemical system: a primary coagulant supplemented by a polyelectrolyte. Two cases seem appropriate: 1) For the operating range of 6-9 pH, an underdosage of primary coagulant is used and is supplemented by addition of a cationic polyelectrolyte. This combination of chemicals broadens the effective pH range of destabilization of curve C in Figure 25, and, additionally, the chemical properties of the polyelectrolyte binds and makes the destabilized particles more adherent to the filter media. 2) For the operating range of 5-7 pH, the polyelectrolyte used to supplement the primary coagulant may be a non-ionic or very weakly anionic. The non-ionic or very weakly anionic polyelectrolyte is useful in systems that tend to modest overdosage situations with primary coagulant. Massive overdosing with



Variation of final zeta potential with pH when treating refinery effluent having negative zeta potential with three levels of coagulant dosage

Figure 28

primary coagulant can be compensated for somewhat by non-ionic or very weakly anionic polyelectrolytes but rapidly blind the filter. These chemical treatments are also useful when high hydraulic loadings are applied to the filter or rapid rate increases occur, both of which may tend to redisperse trapped solids and cause premature breakthrough.

Strong, or very strong, anionic polymers have always performed decidedly poorest in our tests comparing cationic, non-ionic, very weakly anionic, weakly anionic, fairly strong anionic, strongly anionic, and very strongly anionic polyelectrolytes. In one instance, we found treatment with only a cationic polyelectrolyte at a less than 1 ppm to outperform all other combinations of chemical treatment for destabilization of suspended matter preparatory to filtration.

Another distinction that may be important is the nature of the colloids to be destabilized: inert materials including clays, silica, coke fines, oil particles, etc., or biocolloids consisting chiefly of bacteria. Amoco's work on colloid destabilization at other refineries has been largely on inerts, or a mixture of colloids predominately inerts with some biocolloids. The work of McLellon et al. (4) and Stumm and Morgan (5) indicates that where principally biocolloids are concerned, stability is less dependent on repulsive electrostatic interactions and relates primarily to the interaction of the hydrophilic surface of the biocolloid with the aqueous solvent. The source of colloid surface charge is through acid-base interactions of ionogenic functional groups. The authors cited (4, 5) conclude that aggregation of biocolloids is by chemical interaction of the hydroxy metallic polymers with the ionogenic groups of the colloid followed by chemical bridging. If the destabilization mechanism for biocolloids is such a special case, the chemical pretreatment may be optimized by emphasizing the use of organic polymers known to form chemical bridges. The optimal chemical pretreatment would then be expected to be a multichemical system:

1. Two Chemical Systems

    a) Optimize pH.

    b) Use a primary coagulant plus an organic cationic polyelectrolyte, or

    c) Use a primary coagulant plus an organic non-ionic or weakly anionic polyelectrolyte.

2. Three Chemical Systems

   a) Optimize pH.

   b) Use a primary coagulant/organic cationic polyelectrolyte/ weakly anionic polyelectrolyte treatment sequence.

SECTION X

OPERATING AND MAINTENANCE COSTS

Routine unit operation has required only about 10 percent of an operator's time on an around-the-clock basis. Abnormal conditions such as high contaminant concentrations with changes in chemical treatability of the water have required non-routine laboratory analyses and technical assistance. The proportionate cost of these expenses has declined with increasing operator experience and with increased emphasis on control of the upstream facilities.

Because of the remote location of the unit, power costs are the only utility expense. Instrument air is furnished by an onsite compressor and all the heat tracing is electrical. The costs shown below are based on $0.0091 per KWH and an average cycle time of three hours.

		$/Day	$/3785 cu m ($10^6$ gal)
Power:			
Filtering 62 HP, 23 hr	9.69		
Backwashing 215 HP, 1 hr	1.46		
Light and Heat 0.5KW	0.11		
		11.26	5.22
Chemicals:			
Alum $39.63 cu m (15¢/gal)	15.01		
Polymer $1.00/Kg (45¢/lb)	8.11		
		23.12	10.75
Labor:			
Operator 10%, 24 hr/da, $5.20/hr	12.48		
Supervision & Technical 75%	9.35		
Overhead 62%	13.53		
		35.36	16.50
Maintenance:			
Estimate 1.1% of cost		3.80	1.76
		73.54	34.23

Chemical cost data have been estimated on the basis of test data because actual long-term experience with polymeric flocculant is not yet available. An average of 341 cu m/hr (1500 gpm) throughput has been assumed with a 20 wppm alum dosage in the summer and 40 wppm alum plus 2 wppm polymeric flocculant during the winter.

Maintenance costs for the first year resulted largely from repairs that were necessary after a shutdown caused by freezing. Additional heat tracing and new bonded valve liners were installed at that time. These should not be recurring expenses. The continuing maintenance expenses consist of instrument maintenance, weatherproofing repair, and pump repair.

Amoco's contribution to the filter bed replacement was not considered normal maintenance costs and was included with the unit construction costs during the last two project quarters. The expenditure pattern for this project is shown in Table 4.

Table 4. YORKTOWN MIXED MEDIA FILTER EXPENDITURE PATTERN

Engineering and construction

Quarter ending	Engineering	Material and equipment rental	Labor	Total
11-30-70	1,304	3,515		4,819
2-28-71	2,128	17,019	1,206	20,353
5-31-71	1,038	58,727	22,827	82,592
8-31-71	576	4,724	10,069	15,369
11-30-71		1,391	922	2,313
2-29-72		47		47
5-31-72				
8-31-72			707	707
11-30-72			706	706
	$5,046	$85,423	$36,437	$126,906

Operation

Quarter ending	Maintenance and operation	Post construction studies & reports	Totals
8-31-71	8,014	22,874	30,888
11-30-71	5,931	11,413	17,344
2-29-72	6,670	9,793	16,463
5-31-72	5,635	9,226	14,861
8-31-72	5,219	5,605	10,824
11-30-72	5,395	5,411	10,806
	$36,864	$64,322	$101,186

SECTION XI

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SECTION XII

APPENDIX A

ANALYTICAL PROCEDURES USED IN PROGRAM

Parameter	Procedure Reference
Oil	AOM #68
Phenolics (Amino-antipyrine)	API 716-53(1)
Suspended Solids, Total	Standard Methods 224C
Suspended Solids, Volatile	Standard Methods 224D
Ammonia	Standard Methods 132A & B
Turbidity	Turbidimeter-HACH Model 1860A
Sulfides	API Method 713-53(1)
Dissolved Oxygen	Standard Methods 218B
BOD_5	Standard Methods 219 4ii
COD	Standard Methods 220

(1) API Method for Sampling and Analysis of Refinery Wastes

APPENDIX B

CHRONOLOGICAL OBSERVATIONS PERTINENT TO THE OPERATION AND STUDY OF THE YORKTOWN MIXED MEDIA FILTER

June 29, 1971

The unit was started up and operated successfully at 6.6 m/hr (2.7 gpm/sq ft) and about .3 m/hr (1 ft/hr) head loss. The inlet turbidity of 13 was 86 percent removed.

August 9, 1971

The unit was partially drained and the filter bed was found to have expanded and was preventing the surface wash arms from rotating. It was later learned that the backwash rate was inadequate and the bed expansion could logically have resulted from a material build-up in the lower layers of media. The surface wash system was deactivated and subsequent backwashes had no surface wash.

September 9, 1971

The surface wash arms were raised about 5 cm (2 in.) to clear the bed and put into routine service.

October 5, 1971

A flooded API separator caused free oil to be carried through the filter during both filtering and backwashing cycles.

October 12, 1971

The bed was drained to obtain media samples. Some of the coal from the southwest corner of the bed had been displaced, leaving an 45.7 cm (18 in.) deep hole in the corner and a mound of coal over the west surface wash arm pivot. About one-third of the bed surface was involved. No sand or ilmenite were visible.

November 29, 1971

New recommendations were received for the backwash rate; the new rate being about 50 percent greater than the originally specified.

December 9, 1971

A temporary baffle was placed in front of the inlet nozzle in an attempt to solve the persistent problem of having coal shifted from the southwest corner to a mound over the west surface wash arm.

December 30, 1971

Adjustments were made to the backwash troughs to equalize flow distribution between the troughs. Two of the troughs had been carrying about 75 percent of the flow.

January 24, 1972

The temporary inlet baffle was replaced by a permanent one which proved to be very effective in stopping the coal displacement.

February 18, 1972

A dedication ceremony was held with enforcement officials from the various agencies and representatives from the news media in attendance.

February 22, 1972

An adjustment was made in the backwash timer to stop the surface wash before the backwash flow started.

April 7, 1972

Several holes were dug in the bed to inspect the media and confirm the media losses.

May 18, 1972

The media loss seemed to have stopped and the surface wash arms were lowered about 20.3 cm (8 in.) so that they were 5 cm (2 in.) above the bed surface as originally specified.

May 31, 1972

The original grant period expired.

June 30, 1972

The bed was probed and sampled by a manufacturer's representative.

July 11, 1972

A 3-month grant extension was requested in order to include data from the bed repair in the final report.

August 21, 1972

The unit was taken out of service to replace the bed.

September 6, 1972

A new, redesigned, bed had been installed and the unit was put into service.

November 22, 1972

A 6-month grant extension was approved.

April 15, 1973

The unit was drained for inspection of the bed and instaliation of a permanent secondary flocculant nozzle. The surface of the media was about 16.5 cm (6.5 in.) below the surface wash arms. Some fine garnet was observed on top of the surface wash support beam.

May 18, 1973

Work on the final report was initiated in order to make project results to date generally available.

Approval was received for a supplemental program aimed at optimizing chemical preconditioning of filter feed during winter operating conditions to be carried out during the period December, 1973 - March, 1974. A supplement to the project report will be issued.

APPENDIX C

YORKTOWN WATER FILTER ROUTINE OPERATING AND INSPECTION DATA
June 29, 1971 to September 1, 1971

	Influent				Effluent			
	Min.	Med.	Max.	Avg.	Min.	Med.	Max.	Avg.
Water rate, cu m/hr	204	273	397	255				
Alum rate, wppm	20.0	20.0	20.0	20.0				
Water temperature, ^{o}C	26.5	27	29.5	27				
Turbidity, JTU	8	19	28	20	0.9	3.4	17	3.2
Oil, mg/l	0	5	54	7	0	0	14	1.9
Phenolics, mg/l	0.1	0.7	6	1.1	0	0.2	1	0.3
Sulfide, mg/l	0	0	4	0.7	0	0	2	0.6
pH	6.9	7.0	7.5	7.1	6.8	6.9	7.3	6.9
Suspended solids, mg/l	2	20	45	18	2	5	20	4.8
Volatile sus. solids, mg/l								
Ammonia, mg/l								
Dissolved Oxygen, mg/l	0.6	2.9	8	3.6	0.5	1.8	6	2.5
BOD_5, mg/l	0	16	182	35	0	18	35	16

Note: The dissolved oxygen, pH, and BOD_5 data from this period were based on only five sets of samples.

APPENDIX D

YORKTOWN WATER FILTER ROUTINE OPERATING AND INSPECTION DATA
September 1, 1971 to December 1, 1971

	Influent				Effluent			
	Min.	Med.	Max.	Avg.	Min.	Med.	Max.	Avg.
Water rate, cu m/hr	250	341	386	330				
Alum rate, wppm	20			24.4				
Water temperature, ^{o}C	10	18	27	20.5				
Turbidity, JTU	8	25	135	32	1.2	3.7	63	6.6
Oil, mg/l	0	7	105	16	0	4	84	8.3
Phenolics, mg/l	0.2	0.7	2.4	0.7	0.1	0.3	2.0	0.45
Sulfide, mg/l	0	1	38	3.1	0	1	34	2.3
pH	6.7	7.0	8.1	7.0	6.5	6.8	7.5	6.9
Suspended solids, mg/l	8	38	79	43	2	6	30	13.6
Volatile sus. solids, mg/l	4	20	72	35	0	4	27	10.1
Ammonia, mg/l	29	54	90	54	28	53	87	53
Dissolved oxygen, mg/l	0	0.6	6	1.4	0.4	1.6	3.8	1.9
BOD_5, mg/l	3	15	43	19	2	7	21	11

APPENDIX E

YORKTOWN WATER FILTER ROUTINE OPERATING AND INSPECTION DATA
December 1, 1971 to March 1, 1972

	Influent				Effluent			
	Min.	Med.	Max.	Avg.	Min.	Med.	Max.	Avg.
Water rate, cu m/hr	238	341	397	332				
Alum rate, wppm	20			29.4				
Water temperature, ^{o}C	5.5	10	16	10.5				
Turbidity, JTU	23	48	260	65	1	16	100	24
Oil, mg/l	2	13	87	16	1	7	67	10
Phenolics, mg/l	0.1	0.3	1.7	0.5	0.1	0.2	1.4	0.4
Sulfide, mg/l	0	1	2	0.9	0	1	1	0.6
pH	6.0	7.4	8.8	7.4	6.0	7.1	8.2	7.2
Suspended solids, mg/l	33	70	104	68	15	36	96	39
Volatile sus. solids, mg/l	25	54	78	50	8	25	66	29
Ammonia, mg/l	24	54	119	55	25	53	126	55
Dissolved oxygen, mg/l	0	2.1	10.3	2.6	0	5.2	10.0	4.2
BOD_5, mg/l	5	10	61	18	4	7	37	11

APPENDIX F

YORKTOWN WATER FILTER ROUTINE OPERATING AND INSPECTION DATA
March 1, 1972 to June 1, 1972

	Influent				Effluent			
	Min.	Med.	Max.	Avg.	Min.	Med.	Max.	Avg.
Water rate, cu m/hr	182	295	386	296				
Alum rate, wppm	20			31.6				
Water temperature, ^{o}C	10	14.5	23	15.5				
Turbidity, JTU	14	58	220	68	1.5	26	200	36
Oil, mg/l	2	13	68	17	0	7	44	13
Phenolics, mg/l	0.2	0.5	18.7	0.9	0	0.3	16.7	0.8
Sulfide, mg/l	0	1	10	1.0	0	0	9	0.5
pH	6.9	7.3	8.9	7.5	6.6	7.1	8.8	7.2
Suspended solids, mg/l	18	56	145	69	11	31	110	38
Volatile sus. solids, mg/l	6	42	94	50	1	28	88	30
Ammonia, mg/l	25	53	79	52	25	52	74	50
Dissolved oxygen, mg/l	0	0	2.5	0.7	0	1.7	5.9	2.0
BOD_5, mg/l	1	23	171	34	1	13	171	30

APPENDIX G

YORKTOWN WATER FILTER ROUTINE OPERATING AND INSPECTION DATA
September 6, 1972 to December 1, 1972

	Influent				Effluent			
	Min.	Med.	Max.	Avg.	Min.	Med.	Max.	Avg.
Water rate, cu m/hr	204	341	386	343				
Alum rate, wppm	20			21.2				
Water temperature, ^{o}C	10.5	18.5	26.5	18.5				
Turbidity, JTU	21	34	50	33	1.6	9	28	11
Oil, mg/l	0	8	54	9	0	4	42	6
Phenolics, mg/l	0.2	0.4	2.0	0.6	0.2	0.3	1.0	0.4
Sulfide, mg/l	0	0	80	0.9	0	0	60	0.4
pH	7.0	7.3	7.7	7.3	6.8	7.1	7.8	7.1
Suspended solids, mg/l	57	90	141	90	17	36	83	42
Volatile sus. solids, mg/l								
Ammonia, mg/l								
Dissolved oxygen, mg/l								
BOD_5, mg/l	9	18	27	18	7	13	16	13

SECTION XIII

ADDENDUM

Review of initial operational data indicated the chief causes of periodically poor filter performance were related to seasonal changes in aerated lagoon performance, colder water temperatures, and other unidentified changes in water quality. Facilities available were not adequate to respond to changed water quality as required to properly chemically condition the water in preparation for filtration. Seasonal deterioration in filter performance occurs during winter; therefore, a winter program was developed emphasizing study of the water chemistry needed to prepare the aerated lagoon effluent for direct filtration, and the plant facilities were operated to quantitatively demonstrate the need for proper water pretreatment. The general program developed was as follows:

1. Determine the effect of primary coagulant over the pH range 6-8.5.

2. Determine the effect of primary coagulant and cationic polymer over the pH range 6-8.5.

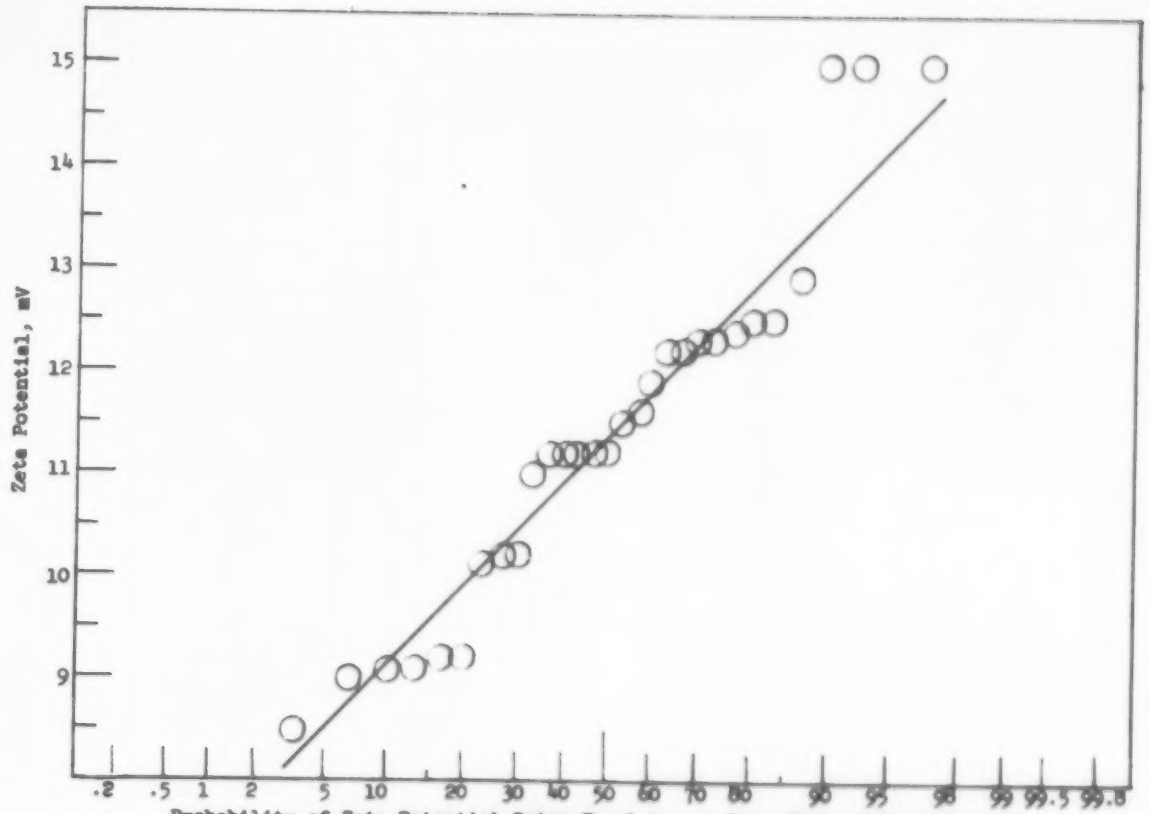
3. Determine the effect of primary coagulant and nonionic and weakly anionic polymers over the pH range of 6-8.5.

4. After determination of the most effective chemical pretreatment per 1, 2, and 3, determine the effect of adding various dosages of powdered carbon at the optimized chemical pretreatment conditions.

5. Determine if the use of powdered carbon is a viable means to "desensitize" the chemical pretreatment such that the charged particles do not have to be so carefully neutralized.

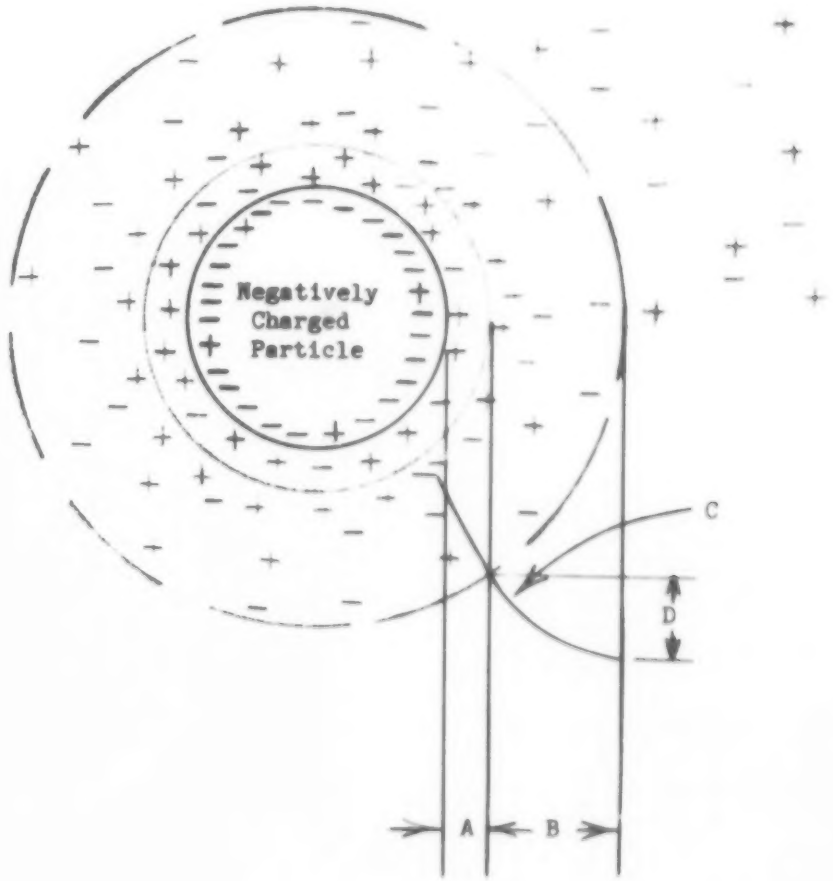
ELECTRICAL CHARGE ON SUSPENDED MATTER IN YORKTOWN AERATED LAGOON EFFLUENT

As the first step in a series of backgrounding studies the zeta potential (ZP) of the suspended matter in the aerated lagoon effluent was determined according to the equipment and method of Riddick (6). A probability plot of these data in Figure 29 indicates the expected average ZP to be about 11.4 mV with a range of 8.5 to 15. The concept of zeta potential is illustrated in Figure 30. In initiating the study using electrical techniques an immediate problem was encountered involving the brackish nature of the effluent. High salt content (8,000-10,000 ppm) resulted in very



Zeta potential distribution of biocolloids in aerated lagoon effluent

Figure 29



A = Rigid Layer Migrating with Particle as Single Kinetic Unit

B = Diffuse Layer of Counterions

C = Electric Potential Surrounding Particle

D = Zeta Potential

Concept of the double layer and zeta potential (after Riddick, 6)

Figure 30

high specific conductivities, requiring use of ancillary automatic sampling equipment with the zeta meter to facilitate measurements of ZP. The brackish nature of the water not only affected the measurement of the ZP but also the interpretation of the measured ZP and the water chemistry for pretreatment. These latter subjects will be discussed in later parts of this section.

SCREENING OF PRIMARY COAGULANTS AND CANDIDATE CATIONIC, NONIONIC, AND WEAKLY ANIONIC POLYELECTROLYTES

Broad water chemistry experience at other Amoco refineries provided background for candidate treatment chemicals and combinations, and screening tests were conducted at the Yorktown refinery using conventional jar test techniques. The results of these initial jar tests were not consistent with typical experience at other Amoco refineries. To focus more accurately on the impact of salinity and temperature, backgrounding tests were conducted at another Amoco refinery having a fresh water aerated lagoon. The effects of temperature and salinity were investigated by adjusting 1) the temperature of fresh sample of aerated lagoon effluent to the desired test temperature and 2) the salinity to various specific conductivities by adding solid NaCl. The jar tests results reflected operating observations at Yorktown; i.e., 1) at warm summertime water temperatures, 26.5+° C (80+° F), salinity effects were minor, but 2) the combination of colder and highly saline water had a more observable effect on the chemical pretreatment requirement for colloidal destabilization. Jar tests indicated that in warm brackish water a two-chemical system at low concentrations was satisfactory whereas for cold brackish water a three-chemical system at higher concentrations was required (see page 62). Polyelectrolytes screen varied widely in effectiveness, and optimizing chemical pretreatment involved testing a series of commercial polyelectrolytes at various combinations until an optimal combination was found. For defining chemical pretreatment requirements for colloidal destabilization and direct filtration, jar tests were useful only for gross screening tests. This was because the results of jar tests were more applicable if "sweep floc" coagulation procedures were used rather than charge neutralization mechanisms. (In a later section, the replacement of jar test techniques by zeta potential measurements to accurately quantify the chemical treatment required will be described.)

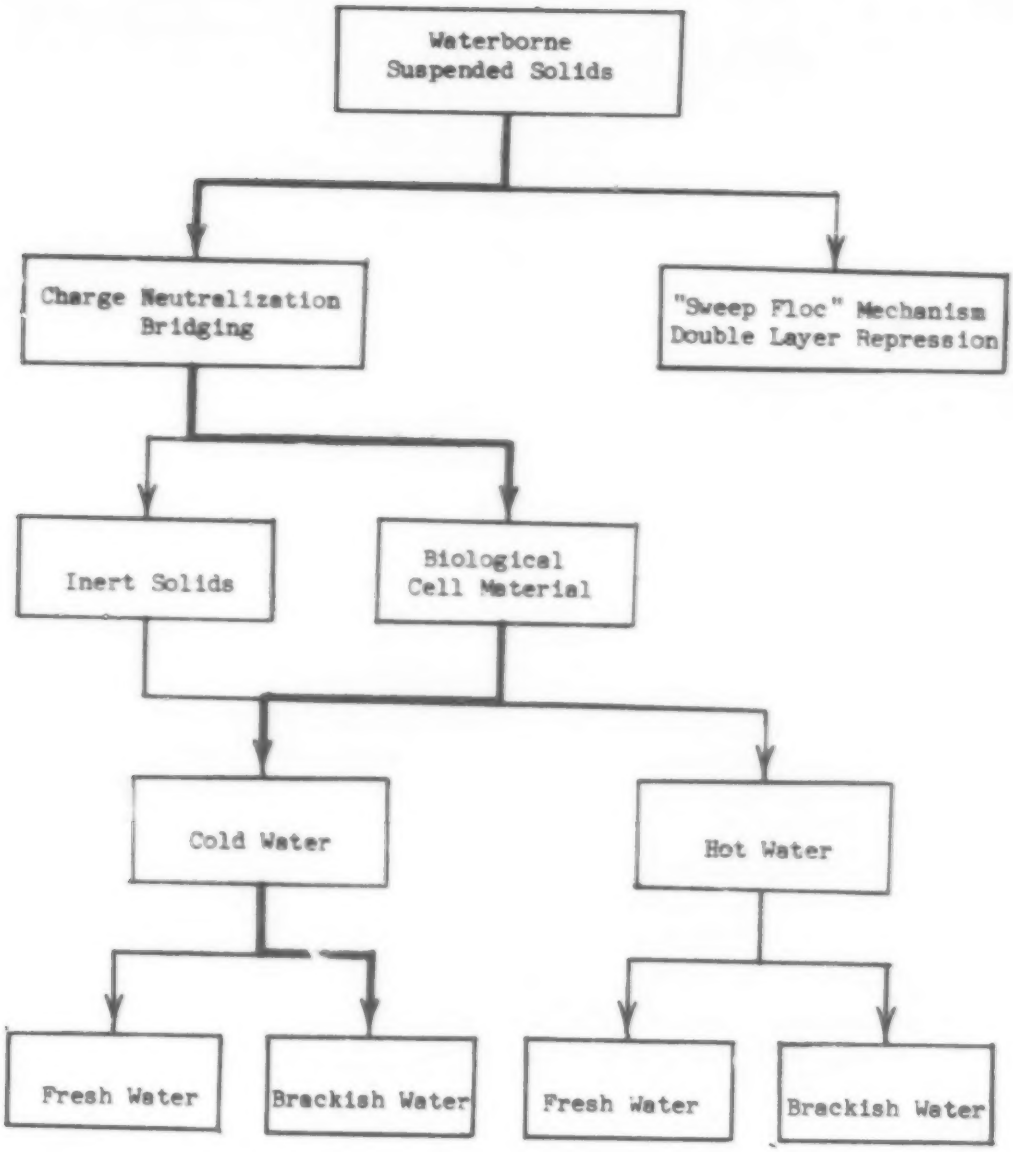
WATER CHEMISTRY

This study pointed out the care with which destabilization chemistry must be approached, identified, and semantics or word usage defined. These points were illustrated by the fact that chemical pretreatment guidelines for direct filtration from fresh water experience had to be further developed for brackish water situations.

Various colloid destabilization mechanisms were illustrated by results of this study. Their identification and description can be discussed in relation to the condition-response schematic for chemical treatment of waterborne colloids outlined in Figure 31. Destabilization of the waterbourne suspended solids may involve four mechanisms: 1) colloid entrapment or removal via the sweep floc mechanism, 2) reduction in surface charge by double layer repression, 3) bridging by polymers, and 4) charge neutralization by adsorption.

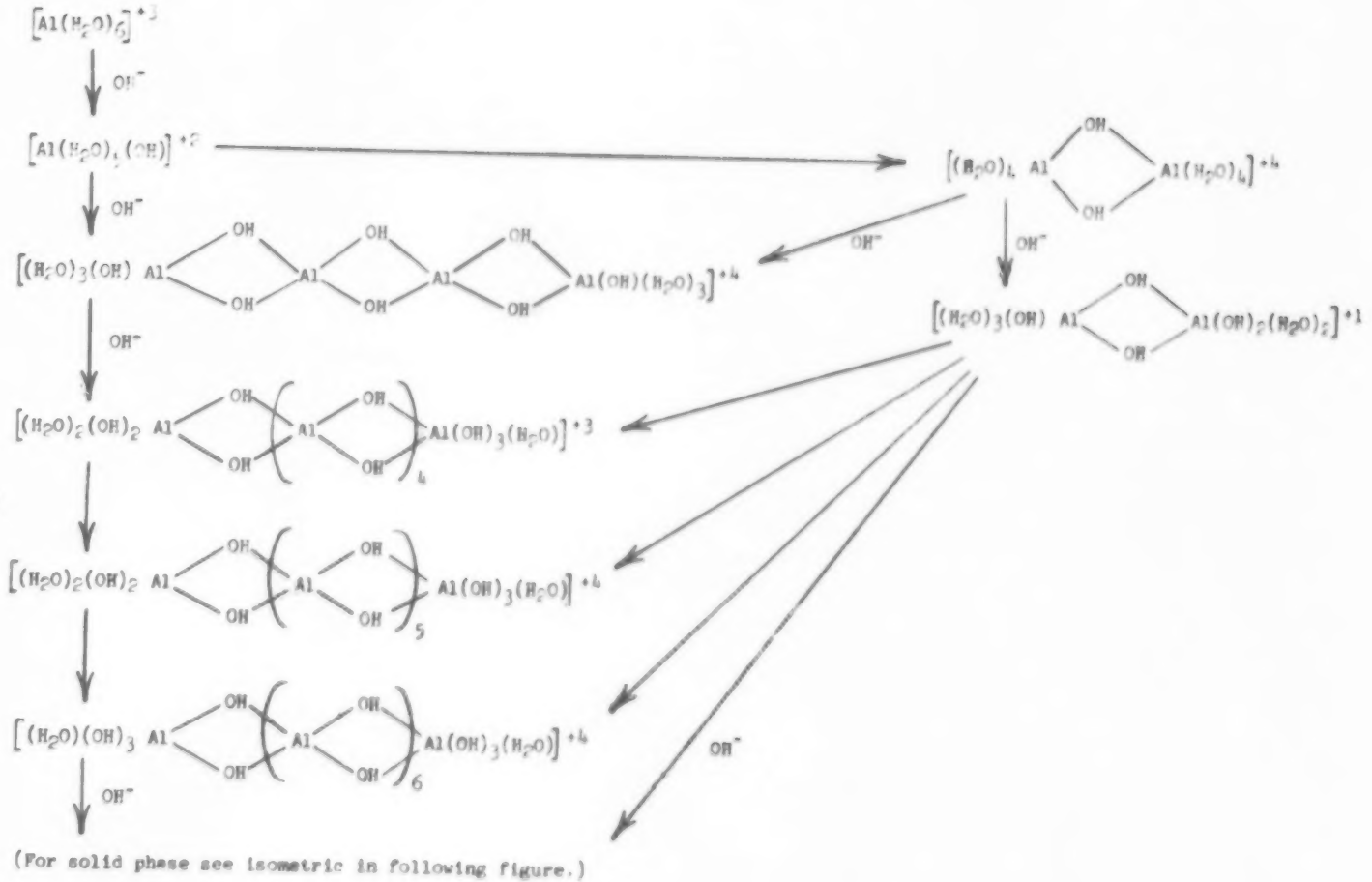
Colloid entrapment involves chemical treatment with comparatively massive amounts of primary coagulants. The amount of coagulant used is typically so great in relation to the amount of colloidal matter that the nature of the colloidal material is not relevant. The amount of primary coagulant used may be 5 to 40 times as much as is used for charge neutralization by adsorption. The rate at which the primary coagulants form hydrous metal oxide polymers (Figure 32) is relatively slow and depends upon water temperature and pH, and coupled with the concentrations used initially, exposes all negatively charged colloidal material to charge neutralization by the transient cationic species. The polymer matrix is 3-dimensional and voluminous, providing for entrapment of solids as shown by Figure 33. As the polymer contracts, freeing solvent water molecules, and settles, the suspended solids remain enmeshed in the settling floc and appear to be swept from the water, hence the description of the process as a "sweep floc" mechanism. This destabilization mechanism is not the subject of this report because it is not applicable to direct filtration. The comparatively massive chemical treatment rapidly blinds the filter causing very short runs.

Reduction in surface charge by double layer repression is caused by the presence of an indifferent electrolyte, which in the case investigated of brackish water treatment was sodium chloride. Riddick (6) summarizes the effect of electrolytes on thickness of the double layer in the data reproduced in Figure 34. For water and monovalent electrolytes, the thickness of the double layer is approximately 10 Angstroms (A°) for 0.1M, 100 A° for 0.001M, and 1000 A° for 0.0001M. For double layer repression of colloid surface charge in brackish waters, the sodium ions of the indifferent electrolyte which surrounds the colloid particles in order to electrically balance their negatively charged surfaces have less tendency to diffuse away from the colloid surface as the salinity increases. Some salt concentration may eventually be reached such that the thickness of the double layer may be small enough that two colloids may approach each other close enough that van der Waals forces cause aggregation. An important aspect



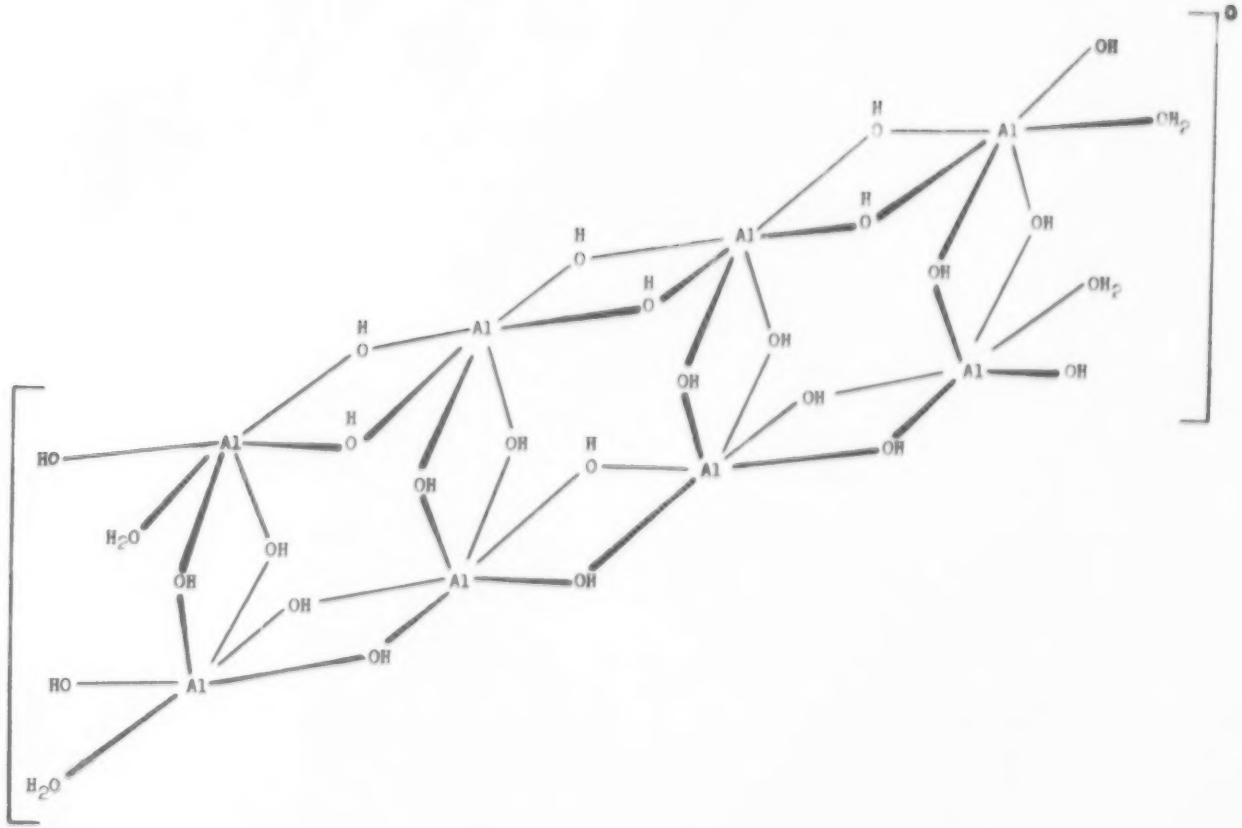
Condition - response schematic for chemical treatment of waterborne colloids

Figure 31



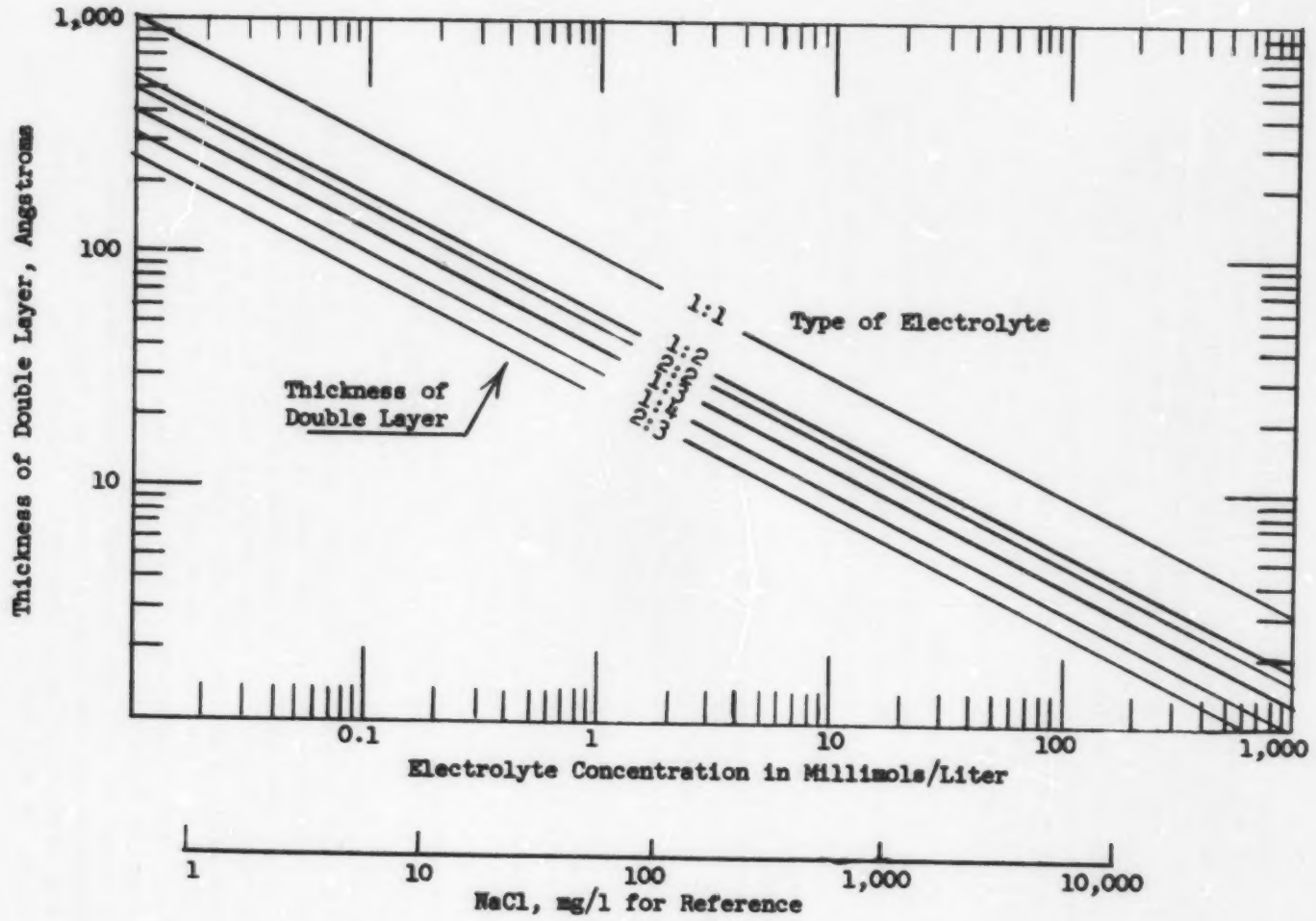
Sequential formation of hydrous aluminum oxide polymers

Figure 32



Example of complex which may exist in precipitated hydrous aluminum oxide polymers

Figure 33



Thickness of the double layer (after Riddick 6)

Figure 34

of double layer repression is that the quantity of colloidal charge is not significantly reduced but just the extent to which it extends out from the colloid surface (Figure 30). This relates to the nature of the destabilizing chemical (salt) and its mode of action; i.e., the sodium ions remain free in the solvent and cause rapid dissipation of the charge as the distance from the colloid surface increases. Double layer repression can improve solids removal by direct filtration, but this mechanism does not achieve the best results and can conceal definition of optimal chemical pretreatment to achieve best filtration results if the interference of this destabilization mechanism is not recognized.

Bridging by polymers describes the destabilization mechanism where the molecules of the added chemical attach onto two or more colloids causing aggregation. Weakly anionic organic polymers are negatively charged; however, they are especially useful for aggregating and binding together aggregates into particles that resist redispersion. Thus, attractive forces of a chemical nature seem to overcome electrostatic repulsion forces due to like charges. Bridging by polymers proved to be an important destabilization mechanism for application to direct filtration. Charge neutralization by adsorption of the destabilizing chemical to the colloid is a key mechanism for optimizing removal of waterborne solids from brackish waters by direct filtration. Perhaps adsorption is a poor word choice here, since the mechanism may not be different from bridging previously discussed. While the mechanism may be the same, the end results are different in that the colloidal charge may not only be reduced to zero but beyond zero, i.e., reversed. Charge neutralization by adsorption infers that the colloid-water interface is changed and thereby its physical chemical properties. This destabilization mechanism can explain those cases where optimal chemical dosages were found and overdosing resulted in a deterioration in, or failure of, direct filtration. Charge neutralization correlated with plant performance as the optimal destabilization mechanism. For plant control of direct filtration, charge neutralization was the key test parameter correlating with performance of the refinery filter when filtering brackish, aerated lagoon effluent. Brackish water required that charge neutralization be measured after dilution with distilled water to separate the effects of double layer repression and charge neutralization; i.e., under plant conditions of high salinity, the addition of destabilization chemicals could reduce the ZP to approximately zero by a range of chemical treatments. However, when double layer repression was the cause of reduced ZP, reduced filter run lengths and performance were observed. Reducing the ZP to approximately zero, as measured by means responsive to charge neutralization,

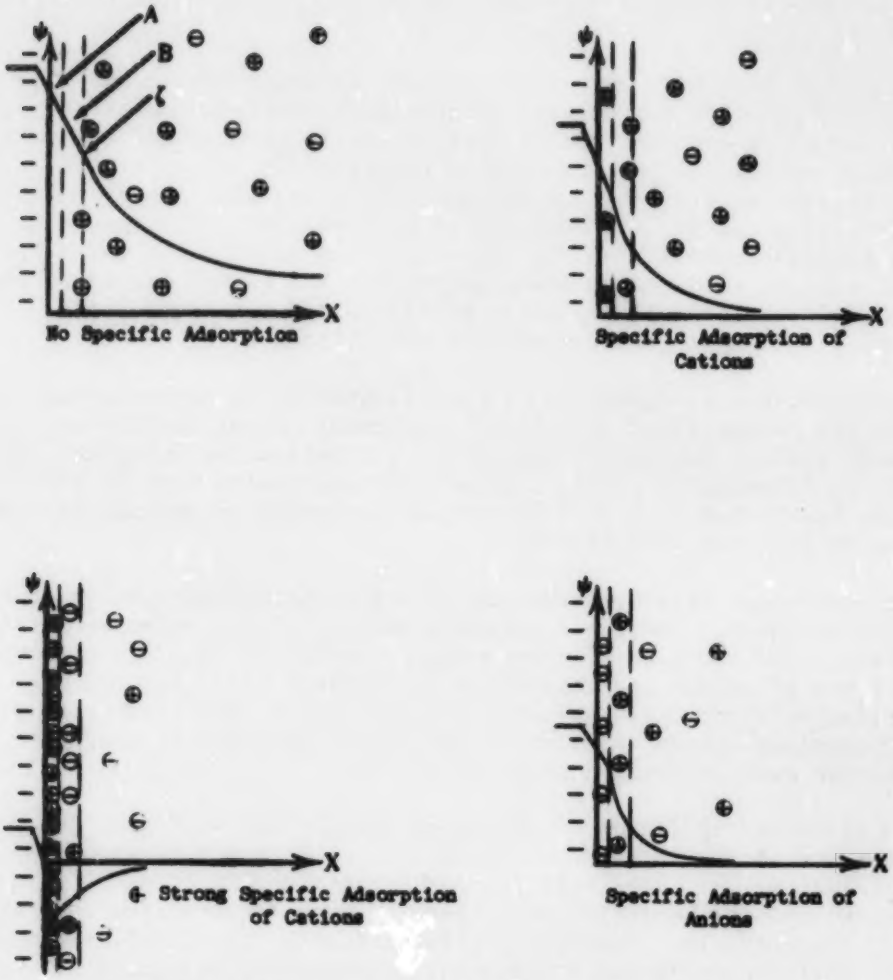
pointed out more definitively the required destabilization treatment and resulted in optimal filter performance. Some examples of charge neutralization mechanisms are shown schematically in Figure 35.

Waterborne colloids subject to chemical destabilization and filtration fall into two general categories: inorganic materials such as clays and sand and organic materials such as bacteria and organic colloids. Both categories of colloidal matter may be stabilized because they are charged and/or are highly hydrophilic. Both categories of colloidal matter also may vary in response to treatment by destabilization chemicals, and within each category, the state of subdivision seems to require additional consideration; i.e., extremely small colloidal particles are sometimes more difficult to aggregate for removal by filtration.

With reference to Figure 31, direct filtration is not concerned with the "sweep floc" or colloid entrapment mechanism for destabilization, but rather charge neutralization and bridging. As will be illustrated later, double layer repression must be carefully identified as a destabilization mechanism or optimal filtration results will not be achieved.

The nature and size distribution of the colloidal material must be addressed next. Inorganic colloids such as clays, silicas, metal oxides, etc. are generally much easier to handle than biocolloids in terms of amount and complexity of chemical treatment required for destabilization. Typically a one-chemical, and occasionally a two-chemical system is required for destabilization of inorganic colloids (see discussion pages 62 and 63).

Double layer repression of charge is illustrated in Figure 36 where the variation in ZP with specific conductance is shown for colloidal silica. The specific conductance and ZP of an 84 mg/l Minusil and salt solution were measured with results of 25,000 and nil, respectively. Successive dilutions with distilled water were made followed by ZP and conductance measurements for Curve A. To a second sample of 8.4 mg/l Minusil, 2.5 mg/l of alum was added, which resulted in a charge reversal on the colloid from about -30 to +30 ZP by adsorption. After alum addition to the second sample, the specific conductance was increased in increments by adding NaCl and measuring ZP and conductance. In both cases, a maximum colloidal charge was observed at a specific conductance of 2,000-3,000. At higher conductivities, the ZP decreased sharply due to double layer repression. In the case of silica, high sodium counterion concentrations eventually achieved almost total reduction in ZP. In the case where the charge on the silica was



A Rigid Layer Migrating with Particle as Single Kinetic Unit

B Slipping or Frictional Boundary Layer of Ions

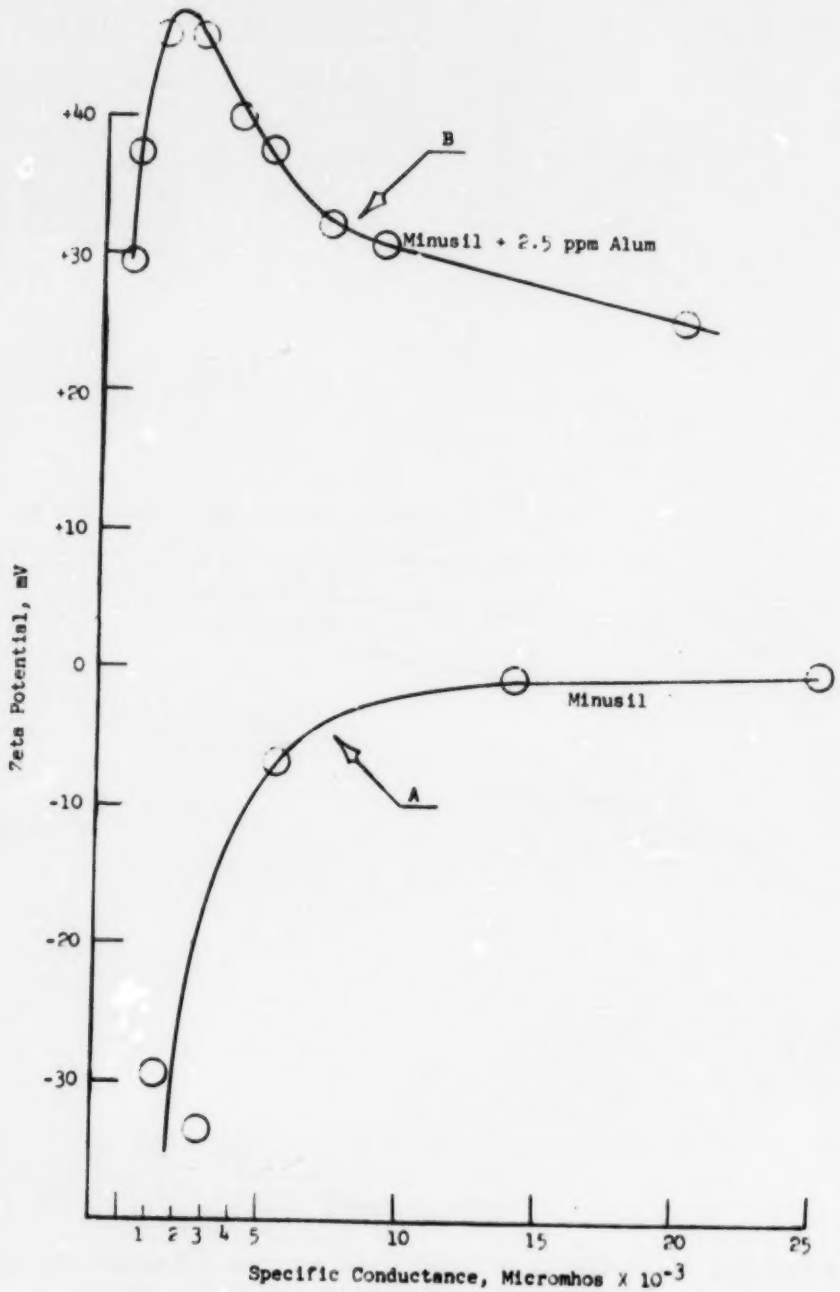
X Distance from An Arbitrary Point Inside Solid Phase

ψ Electrical Potential

ζ Zeta or Electrophoretic Potential

Distribution of ions and potentials in the double layer surrounding colloids (after Overbeek 7)

Figure 35

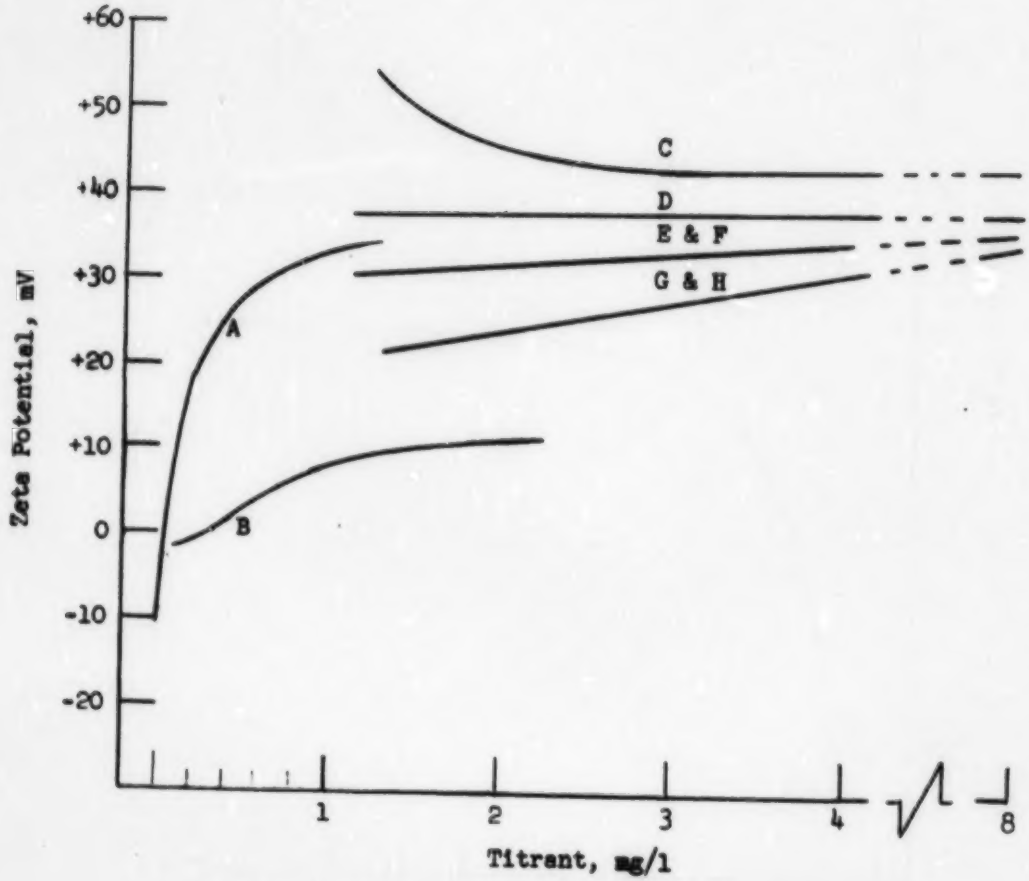


Variation of charge on Minusil with specific conductance

Figure 36

Titration of 8.4 ppm Minusil at Indicated Specific Conductance and Titrant

Curve	Specific Cond.	Titrant
A	2,850	Alum
B	12,000	Alum
C	8.5	Cationic PE E-32
D	15,500	Cationic PE E-32
E	8.0	Cationic PE 573
F	15,500	Cationic PE 573
G	7.5	Cationic PE E-5
H	15,000	Cationic PE E-5



Variation of charge on Minusil with various titrants and two levels of specific conductance for each titrant

Figure 37

reversed by adding alum, the colloid-water interface was obviously changed in physico-chemical properties and/or the chloride counter-ion was not as effective for double layer repression as was sodium.

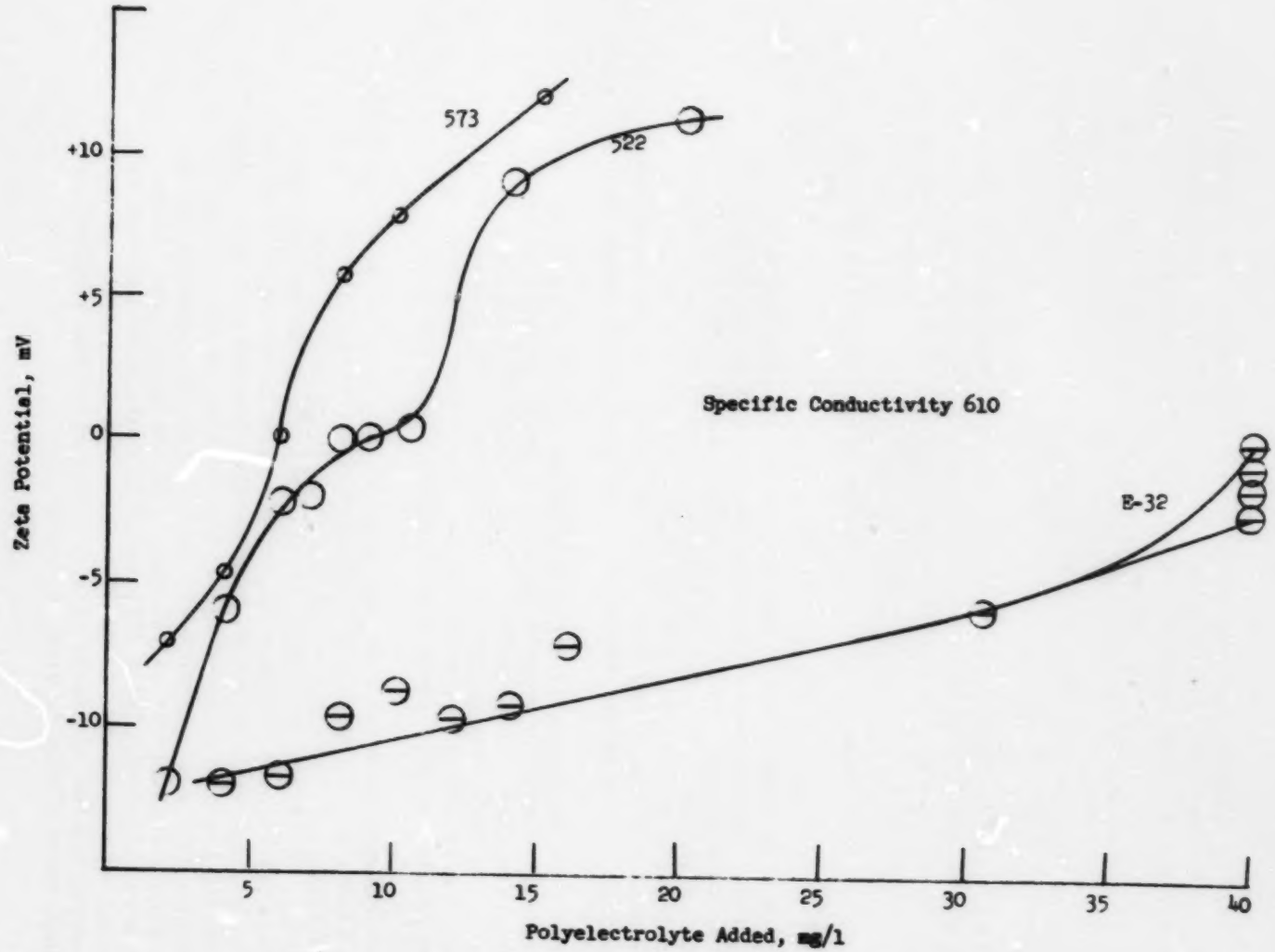
Further ZP measurements using silica and determining the effect of specific conductance on the performance of various organic cationic polyelectrolytes and alum are shown in Figure 37. Again, specific conductance was changed by adding solid NaCl.

Curves A and B (Figure 37) indicate titration with alum at two levels of specific conductance, 2,850 and 12,000, respectively. Even 2,850 is high since refinery effluents with only fresh water inputs are well under 1,000. At the higher specific conductance, the increased electrolyte impacts on the intensity of charge reversal achievable by alum and on the stoichiometry to achieve zero ZP.

The results suggest anion penetration of the alum polymer by chloride. Anion penetration, the replacement of a coordinated group such as aquo, hydroxo, or another anion, can be visualized with reference to Figures 32 and 33. With reference to Figure 32, penetration by chloride ion may impair the olation of alum to polymers and reduce the formation, or charge, of the transient cationic alum polymers important to colloid charge reduction.

Other data on Figure 37 are ZP-titration curves using three commercially available organic cationic polyelectrolytes at two conductivities. On polyelectrolytes 573 and E-5 the salt did not impact on their charge reversal properties. For polyelectrolyte E-32 a salt effect was observed, but the extent of charge reversal was greater in both cases than achieved by 573 and E-5.

For contrast with the data for destabilization of inorganic colloids, a series of tests were run to determine the effectiveness of destabilization chemicals on biocolloids in fresh and brackish water. ZP-titration curves for refinery, fresh water (specific conductivity 610), aerated lagoon biocolloids are shown in Figure 38. One immediately interesting observation was that E-32, which reversed the charge of the inorganic colloid to the highest ZP (Figure 37), was comparatively ineffective for reducing and reversing the charge on biocolloids. On the other hand, other organic polyelectrolytes (573 and 522) could effect charge reversal of biocolloids in fresh water. The inferiority of E-32 for destabilization of biocolloids for filtration was verified in plant tests (Table 5, runs 26 and 27).



The variation in zeta potential of particles in aerated lagoon effluent (fresh water) with addition of cationic polyelectrolytes

Figure 38

Table 5. A PARTIAL LIST OF PLANT TESTS

Run	m/hr	gpm/sq ft	Concentration, mg/l Alum	Cationic	Nonionic or Anionic	Comments
1	12.2	(5)	21	8 (522)	0	Early breakthrough
2	12.2	(5)	10	8 (522)	0	Early breakthrough
3	12.2	(5)	0	8 (522)	0	Very poor
4	12.2	(5)	20	0	0	Poor
5	12.2	(5)	20	0	.1 (905)	Poor
6	12.2	(5)	10	0	.1 (905)	Poor
7	12.2	(5)	20	0	.1 (905)	Poor
8	12.2	(5)	20	4 (573)	0	Poor, early breakthrough
9	12.2	(5)	15	4 (573)	.007 (905)	Poor
10	12.2	(5)	20	15 (522)	.1 (2700)	Good, 1.3 hours to breakthrough
11	12.2	(5)	20	4.5 (522)	.1 (2700)	Fair, 1.0 hours to breakthrough
12	12.2	(5)	20	0	0	Poor, .2-.3 hours
13	12.2	(5)	20	0	.11 (2700)	.65 hours
14	12.2	(5)	20	0	.1 (2700)	.65 hours
15	8.6	(3.5)	20	0	0	1.5 hours, fair at this loading
16	8.6	(3.5)	20	0	.17 (2700)	Fair, 2 hours
17	8.6	(3.5)	20	9 (522)	.17 (2700)	Good, 3.5 hours
18	8.6	(3.5)	20	9 (573)	.14 (2700)	2.5 hours
19	8.6	(3.5)	35	3 (573)	.17 (2700)	Fair, 1.5 hours
20	8.6	(3.5)	10	15 (573)	.157 (2700)	2.75 hours
21	8.6	(3.5)	20	16 (573)	.157 (2700)	3.0 hours
22	8.6	(3.5)	0	15 (522)	.16 (2700)	1.25 hours
23	8.6	(3.5)	0	17 (522)	.17 (2700)	2.25 hours
24	8.6	(3.5)	20	0	0	Very poor
25	8.6	(3.5)	20	0	.3 (2700)	Poor
26	8.6	(3.5)	20	10 (E-32)	0	Very poor
27	8.6	(3.5)	20	10 (E-32)	.3 (1110)	Poor
28	8.6	(3.5)	20	0	.3 (1110)	0.9 hours
29	13.9	(5.67)	20	15 (522)	.3 (1110)	0.9 hours, better at this loading

Chemicals:
522 = Betz DK522 (Cationic)
573 = American Cyanamid (Cationic)
E-32 = Armak (Cationic)
905 = American Cyanamid (Nonionic)
2700 = Calgon WT 2700 (Weakly Anionic)
1110 = Betz 1110 (Weakly Anionic)

The impact of specific conductance (salinity) on biocolloid destabilization is shown in Figure 39. Curve E shows the impact of increasing salinity on the ZP of biocolloids in fresh water, aerated lagoon effluent. The initial specific conductance of 610 was increased by adding solid NaCl and measuring the ZP. This double layer repression of ZP yields a curve similar to E-32 in Figure 38, which may yield a clue to the biocolloid destabilization mechanism of E-32 and why it is not effective. Curves A and B in Figure 39 are replots of fresh water data in Figure 38 for the purpose of comparing to brackish water data in curves C and D. Curves C and D were developed by taking a fresh water, aerated lagoon sample, adding solid NaCl to give a specific conductance of 12,000 and immediately running a ZP-titration curve. The initial ZP of the biocolloids was only very slightly negative due to double layer repression by the salt. Two very interesting and revealing observations from curves C and D are: 1) for curve C, the salt approximately halved the effectiveness of cationic polyelectrolyte 573 for reversing the ZP of the biocolloids to about +3 ZP, and 2) for curve D, the salt completely destroyed the effectiveness of cationic polyelectrolyte 522 for reversing the ZP of the biocolloids. In fresh water, 522 was very effective for reversing the ZP of biocolloids (Figure 38).

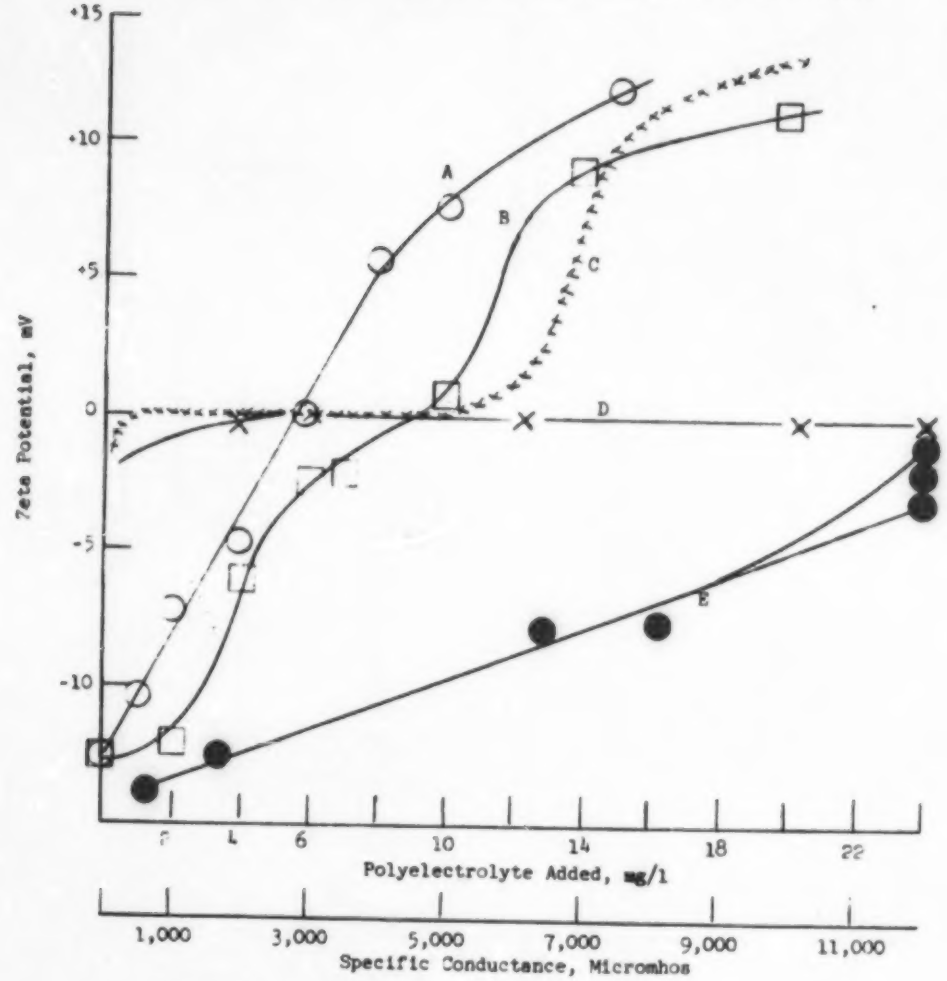
For fresh water colloidal systems, jar tests and plant experience at refineries have demonstrated the importance of pH for the evaluation of chemical destabilization systems. Jar tests on the brackish aerated lagoon effluent at the Yorktown refinery did not reflect the pH response that fresh water systems did; therefore, this aspect of the destabilization chemistry was investigated further.

ZP-alum titration curves on biocolloids in brackish aerated lagoon effluent were run at a constant pH of 6.0 and 8.5. These data are plotted in Figure 40 and show that 1) at a pH of 8.5, alum has an insignificant impact on the ZP of biocolloids in brackish water, and 2) in contrast to fresh water experience, alum does not appreciably affect the ZP at a pH of 6.0. The data for brackish water at 6 pH again suggest that in brackish water, anion penetration of the alum polymer severely interferes with olation of alum and its ability to reverse the ZP. Qualitatively, more acidic conditions resulted in more reduction of ZP with alum addition, but quantitatively the effect was not as pronounced as in fresh water.

The nature of biocolloids in aerated lagoon effluent reflect their environment. The ZP of the brackish aerated lagoon effluent

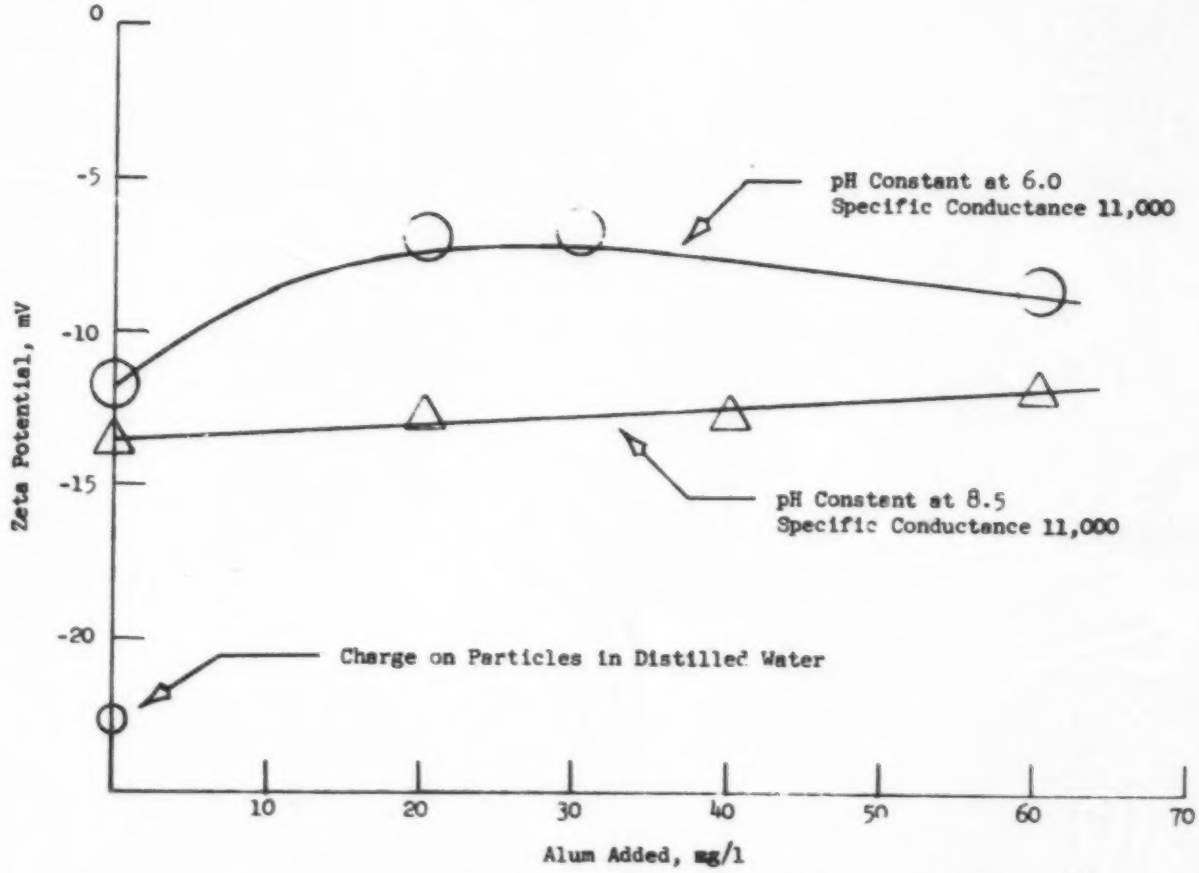
Key

A = Addition of Cationic 573 at Specific Conductance of 610
B = Addition of Cationic 522 at Specific Conductance of 610
C = Addition of Cationic 573 at Specific Conductance of 12,000
D = Addition of Cationic 522 at Specific Conductance of 12,000
E = Addition of NaCl(s) to Give Indicated Specific Conductance



Variation of charge on particles in fresh water aerated lagoon effluent with addition of various polyelectrolytes and NaCl

Figure 39



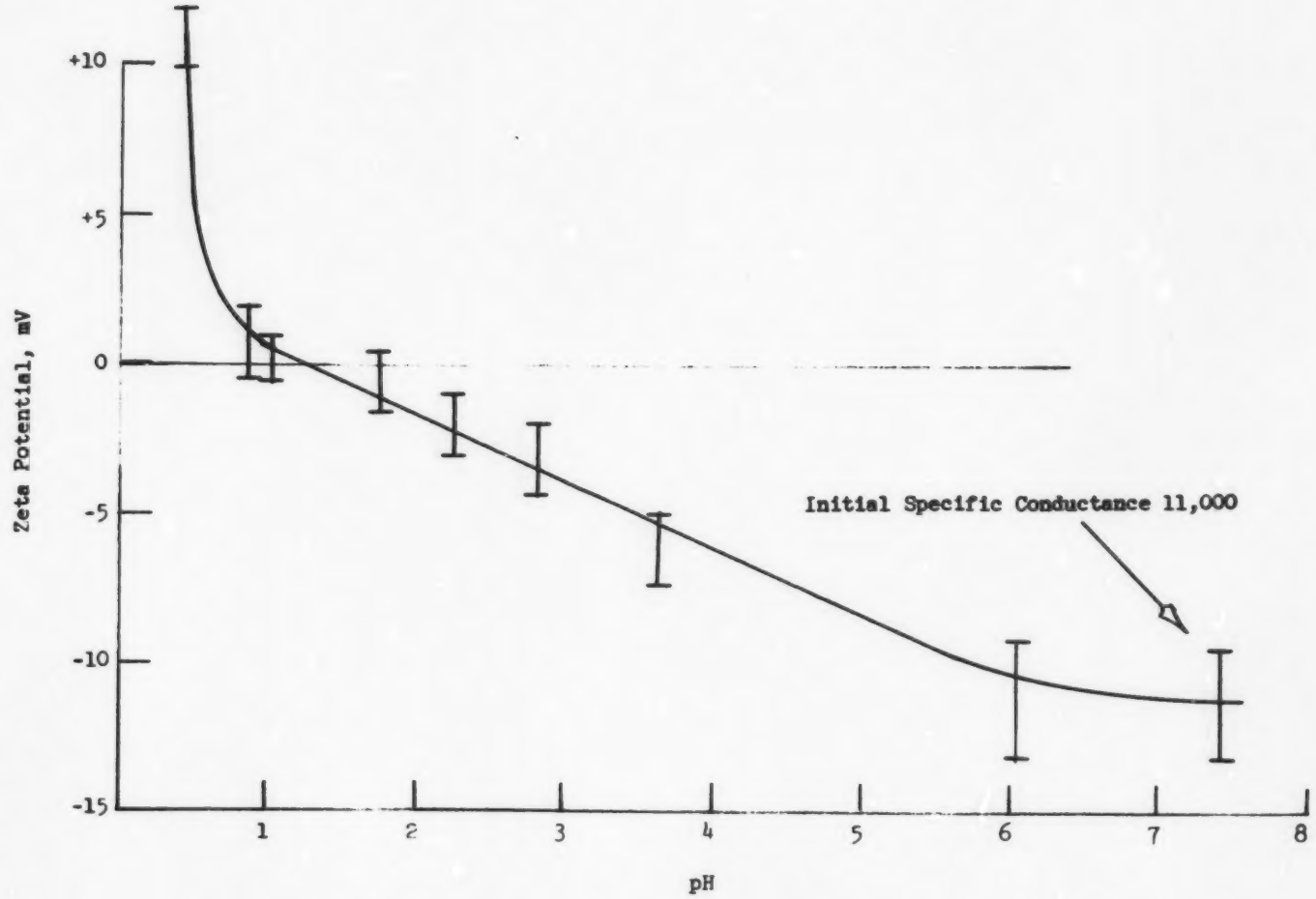
The variation in zeta potential of particles in aerated lagoon effluent with alum at pH of 6.0 and 8.5

Figure 40

averaged -11.4 mV and ranged from -8.5 to -15 as shown in Figure 29. When biocolloids were removed from brackish water by millipore filtration and redispersed in distilled water, the ZP intensified to -23. The ZP of brackish aerated lagoon biocolloids responded to pH as shown in Figure 41, a curve characteristic of biocolloids. Biocolloids in fresh water aerated lagoons had a ZP distribution similar to brackish water biocolloids; however, when their environment was changed by adding salt, the ZP could be decreased to almost zero (Figure 39). Plant-scale filter tests conducted concurrent with laboratory investigations indicated that early breakthrough of solids was characterized by having a significant negative ZP. Pretreatment with a three-chemical destabilizing system could achieve essentially zero ZP, but differences in filtration performance would occur between essentially the same colloidal system treated to zero ZP with different chemical treatments.

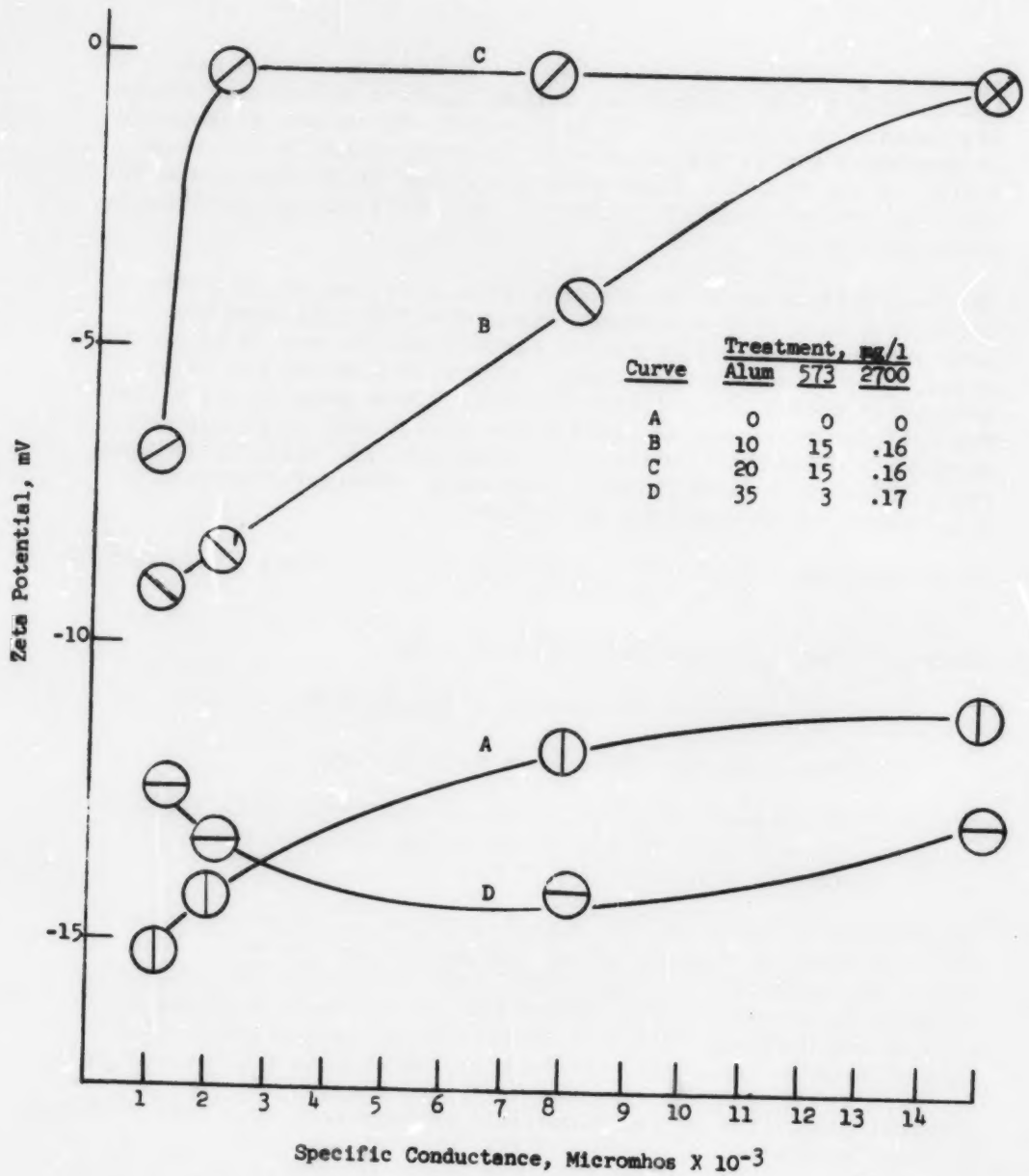
Differences in plant performance of chemical destabilization systems relate to the destabilization mechanism and the requirements of the colloidal system. Shown in Figure 42 are data that permit these differences to be identified and the optimum chemical destabilization system determined. These curves and interpretations were developed by measuring the ZP of brackish feed to the plant filter with an initial specific conductivity of 15,000 and various chemical treatments and by following plant filter performance. Each sample was successively diluted with distilled water and the ZP and conductivity determined with each dilution; i.e., the curves are read from right to left. Curve A shows the response to salinity of the untreated biocolloids. As the salinity decreases, the repression of the double layer decreases and the charge of the ZP intensifies to less than -15 mV. Curve B shows the response of the biocolloid system to dilution when treated by 10 mg/l alum, 15 mg/l cationic PE 73, and 0.16 mg/l anionic PE 2700. Initially, the ZP was approximately zero at a specific conductance of 15,000. Upon dilution, however, a negative ZP rapidly developed. This suggests that some of the charge reduction to achieve satisfactory plant operations had not been achieved. Curve C shows that increasing the concentration of the alum component of the three-chemical system for Curve B increases significantly the amount of destabilization by charge neutralization. Increasing the alum component further and decreasing the amount of cationic polyelectrolyte in the three-chemical system resulted in a completely ineffective treatment for destabilization (Curve D).

Thus, for biocolloids in brackish waters, using ZP to determine optimal chemical treatment requires that ZP be measured at low,



Charge on suspended matter in aerated lagoon effluent as a function of pH

Figure 41



Curve	Treatment, mg/l Alum	573	2700
A	0	0	0
B	10	15	.16
C	20	15	.16
D	35	3	.17

The variation of charge on aerated lagoon particles with specific conductance after treatment by various chemical combinations

Figure 42

specific conductance (by dilution) to insure that charge neutralization is the predominate destabilization mechanism. Charge neutralization results in the most stable, filterable aggregates of suspended matter most resistant to redispersion by hydraulic forces in the filter. These interpretations of ZP data and evaluation of optimal chemical treatment were confirmed by simultaneous plant test data.

The destabilization of biocolloids in brackish water therefore requires a carefully determined three-chemical treatment preparatory to direct filtration if optimal results are to be achieved; a one, two, or non-optimal three-chemical system results in significantly poorer plant filter results. These data indicate that the colloid system has at least three components: one responsive to alum; a second responsive to certain cationic polyelectrolytes; and a third responsive to both. The total chemical treatment requirement can be outlined as follows:

Total Chemical = (Alum)(X) + (cationic PE)(Y) + (Alum + Cationic PE)(Z) + Anionic (k)

Where X = that component responsive to Alum,

Y = that component responsive to cationic PE,

Z = that component responsive to both, and

k = the overall requirement of the destabilized colloids for a weakly anionic PE to resist redispersive hydraulic forces in the filter.

The functional mechanism for destabilization of biocolloids in brackish water by three-chemical systems is not obvious. Data in Figure 40 indicate that under these conditions alum is a very poor prospect for chemical destabilization; yet, alum is required as part of the chemical treatment system for optimal results. The role of alum is not clear. Perhaps it reacts with the biocolloid fraction not responsive to cationic PE and changes the physicochemical properties of the biocolloid surface such that this fraction is then responsive.

The third chemical component of the required treatment is also somewhat unusual in that the conventional nonionic polyelectrolyte widely used as a filter aid is not effective; weakly anionic polyelectrolytes are required.

Laboratory ZP data for various chemical treatment systems were supplemented with plant performance data to aid in interpreting laboratory observations. Typical plant data accumulated for each test period are illustrated in Figure 43. Run length comparisons were determined as the time when the filter effluent reached 10 JTU. A partial list of plant runs is shown in Table 5, page 93.

Guidelines for the filtration of biocolloids in brackish water can be summarized as follows:

1. Warm water conditions, 29.5+° C (85+° F), require relatively simple chemical pretreatment systems and permit higher hydraulic loadings.

2. The colder the water conditions the more important and complex the chemical pretreatment.

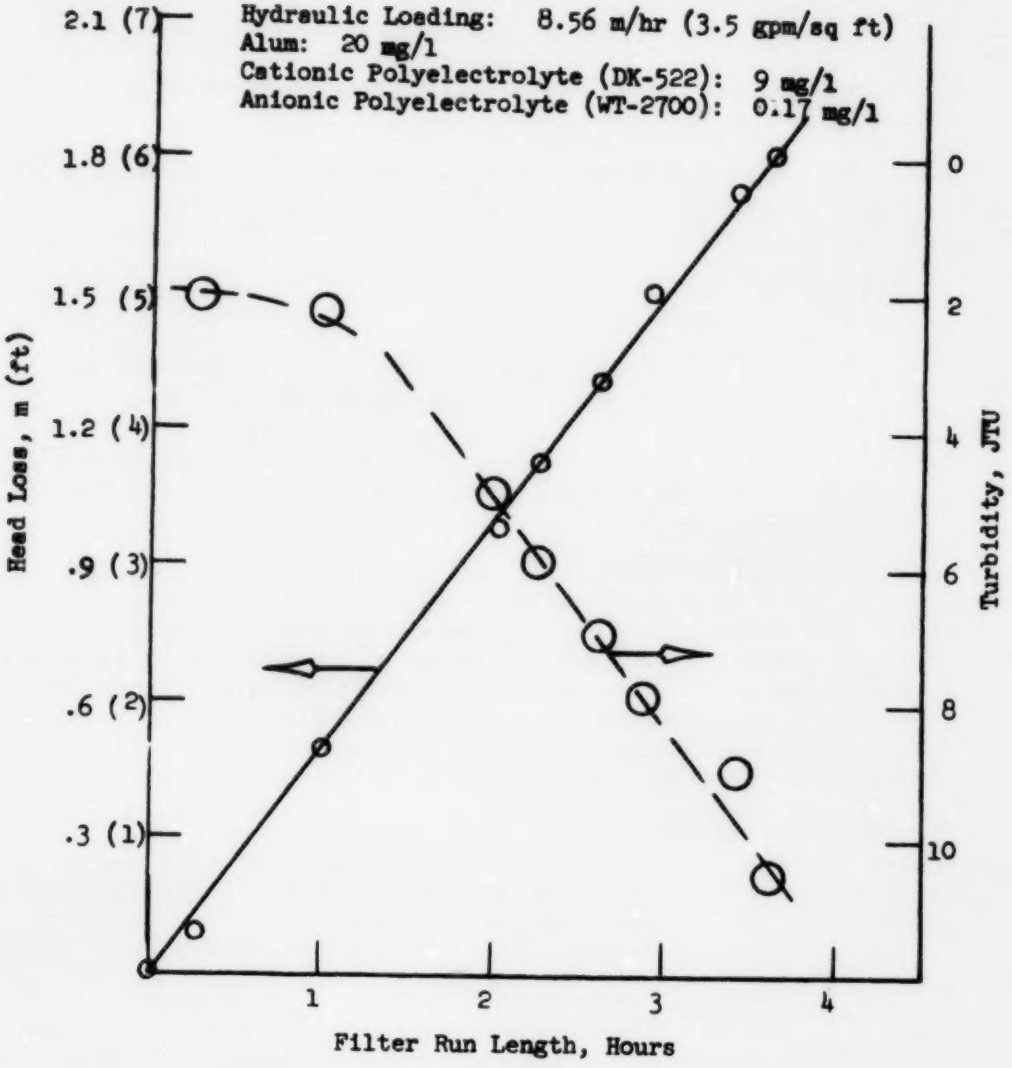
3. Even with optimized chemical pretreatment, in colder water the filter hydraulic loading must be decreased.

4. The filter hydraulic loading as a function of water temperature recommended in Figure 44 also relates to water viscosity.

Powdered activated carbon (PAC) was incorporated into the optimized chemical treatment system at levels of 50, 100, and 150 mg/l. No "desensitizing" of the biocolloid treatment system was observed; indeed, if an effect existed at these levels of treatment, it would appear to be one of interference. PAC samples from four vendors were screened and similar effects observed. All of the PAC used had a substantial negative zeta potential which may have increased the destabilization chemical requirement.

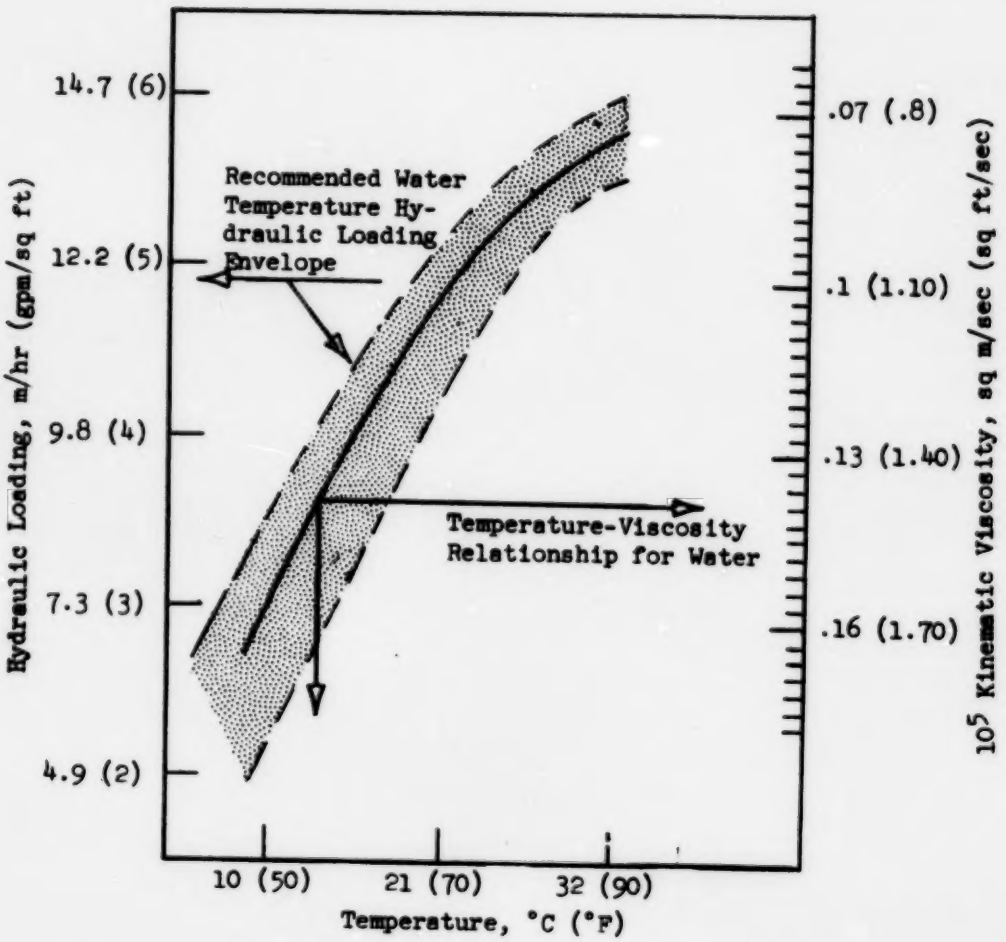
APPLICATION OF RESULTS

The method for determining the optimum chemical treatment for destabilization of colloidal systems was applied at other Amoco refineries. Using temporary, make-shift chemical addition facilities plant tests were run. In all cases, including the use of both filters and dissolved air flotation units for phase removal, the improvement in unit operation was excellent. As a result of these favorable plant tests, the Yorktown filter is being retrofitted with the required chemical addition facilities as are new facilities under construction at Amoco's Texas City refinery. Startup of both these facilities is anticipated to be in April, 1975. The continuous, long-term operation of these facilities is needed to provide a measure of performance which can be sustained in the treatment of industrial effluents when the water chemistry requirements are met.



Head loss - turbidity breakthrough curve
filtering chemically treated aerated lagoon effluent

Figure 43



Recommended hydraulic loading rates as a function of water temperatures and showing the correlation with water viscosity

Figure 44